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ORGANOTIN DERIVATIVES OF MANGANESE
AND RHENIUM CARBONYLS

BY

JOHN ANTHONY JEFFREY THOMPSON

A THESIS

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The undersigned certify that they have read and recommended to the Faculty of Graduates Studies for acceptance a thesis entitled

ORGANOTIN DERIVATIVES OF MANGANESE
AND RHENIUM CARBONYLS

submitted by JOHN ANTHONY JEFFREY THOMPSON in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Compounds of the general types $R_3SnM(CO)_5$, $R_2Sn[M(CO)_5]_2$ and $RSn[M(CO)_5]_3$ ($R = CH_3$, C_6H_5 , $n-C_4H_9$ or $CH_2 = CH$; $M = Mn$ or Re) have been synthesized by the reactions of the sodium salt of $M(CO)_5^-$ with organotin chlorides.

A number of derivatives of the metal-metal bond compounds have been obtained by replacement of chloride in $(C_6H_5)_nCl_{3-n}SnMn(CO)_5$ ($n = 0, 1, 2$). Thus, reaction of C_6F_5Li or C_6F_5MgBr yielded derivatives of the type $(C_6H_5)_n(C_6F_5)_{3-n}SnMn(CO)_5$. Reaction of $(C_6H_5)_2ClSnMn(CO)_5$ with C_6F_5Li also gave the ditin derivative, $[(C_6H_5)_2SnMn(CO)_5]_2$.

Compounds containing S-Sn-M linkages were prepared by reaction of $R_nCl_{3-n}SnM(CO)_5$ and $Cl_2Sn[M(CO)_5]_2$ with RSH ($R = CH_3$, C_6H_5 , C_6F_5) in the presence of triethylamine. Heterocyclic sulfur-tin derivatives were obtained by reaction of dithiols, $HS(CH_2)_nSH$ ($n = 2, 3$) and $HSCH(CH_3)-CH_2SH$ with dichlorotin compounds. Three compounds containing tin atoms bridged by sulfur atoms are reported also.

Preparation of the phosphine derivatives $[(C_6F_5)(C_6H_5)_2P]Mn(CO)_4]_2$ and $[(C_6F_5)(C_6H_5)_2P]Mn_2(CO)_9$ is described. Cleavage of the Mn-Mn bond of the former compound with sodium amalgam gave the salt $NaMn(CO)_4[P(C_6H_5)_2(C_6F_5)]$,

from which $(C_6H_5)_3SnMn(CO)_4[P(C_6H_5)_2C_6F_5]$ was prepared. Reaction of this product with HCl yielded the Cl_3Sn -derivative.

The infrared spectra of the carbonyl stretching region were recorded for all compounds. For the mono (metal carbonyl) species, three or four absorptions were observed. Bands were assigned on the basis of idealized C_{4v} symmetry, and carbonyl stretching force constants were calculated using the Cotton-Kraihanzel approximation. Infrared spectra for the bis- and tris- metal carbonyl derivatives indicate that the "local symmetry" method does not correctly predict the number of infrared-active bands. This is a result of coupling of carbonyl modes on different transition metal atoms, which may take place across several intervening atoms.

The carbonyl stretching frequencies of $R_nX_{3-n}SnMn(CO)_5$ ($X = \text{halogen}$) were observed to increase linearly with the sum of the electronegativities of the halide substituents. Using this fact, values for the electronegativities of the C_6F_5 and C_6F_5S groups have been estimated.

Proton nmr spectra for methyltin and methylthiotin derivatives were recorded. Substituents effects on the values of the chemical shifts and proton-tin coupling constants are discussed.

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CHAPTER I

INTRODUCTION

Although organotin chemistry is more than a century old, it has been only in the last 15 or 20 years that interest in the field has become extensive. Since 1960, interest in the ability of organotin groups to bond to transition and other main-group metals has burgeoned.

As it first presented itself, the problem in this present work involved the preparation and study of multi-nuclear tin-manganese and tin-rhenium compounds, with emphasis on the metal-metal bonding. However, during the course of the work, it became apparent that the chemistry of tin as it existed in these compounds was of extreme interest. Syntheses were therefore extended to include compounds in which a large number of different substituents were bonded to tin. This Dissertation describes the preparation and spectroscopic studies of these compounds and represents a contribution both to organotin chemistry and to our knowledge of metal-metal bonding.

A. Metal-Metal Bonds Involving Tin

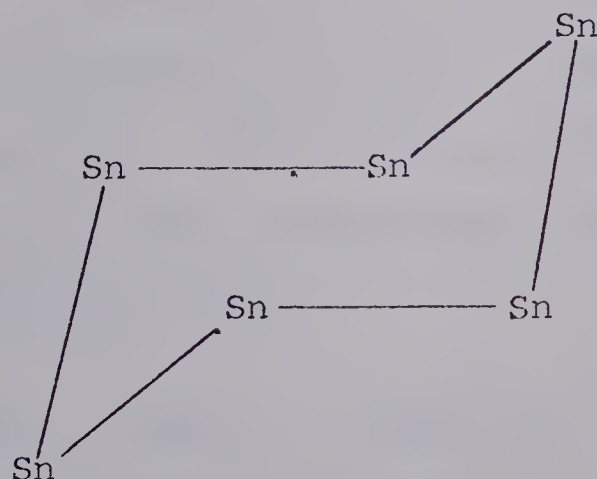
Because of the long history of organotin chemistry, it is impossible to cover even a fraction of the literature on the subject in this discussion. An exhaustive review by Ingham, Rosenberg and Gilman (1), containing 924

references up to 1960, provides an excellent survey.

Here, discussion will be limited to the history of the Sn-M bond where M can be tin itself, another main-group IV metal or a transition metal.

Bonds between two tin atoms were first suspected by Rügheimer (2) in 1909 for $[(C_2H_5)_3Sn]_2$ and later by Kraus and Sessions (3) in 1925 for the hexamethyl species. However, in both cases these compounds were considered to be dimers of the trivalent free radical species $(C_2H_5)_3Sn$ and $(CH_3)_3Sn$. In the latter case the compound was actually referred to as the "free trimethyltin group", which was considered to exist in benzene solutions (3). From " $(CH_3)_3Sn$ ", Kraus and Sessions prepared the sodio-derivative, $(CH_3)_3SnNa$, which upon reaction with triethyltin chloride yielded what was formulated as a ditin compound, $(CH_3)_3Sn-Sn(C_2H_5)_3$. The free $(CH_3)_3Sn$ species was accepted for several years. In 1941, however, Morris and Selwood (4) proved that the compound was actually hexamethylditin by magnetic susceptibility measurements and a redetermination of the molecular weight. In benzene solution at 90°C only 2% dissociation was detected. With the advent of nmr spectroscopy, the existence of the dimer was confirmed (5) by the observation of two sets of methyl-tin couplings due to the α and β tin atoms.

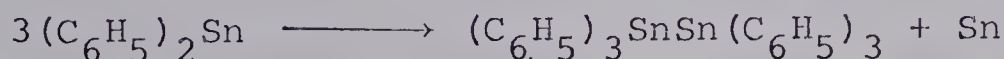
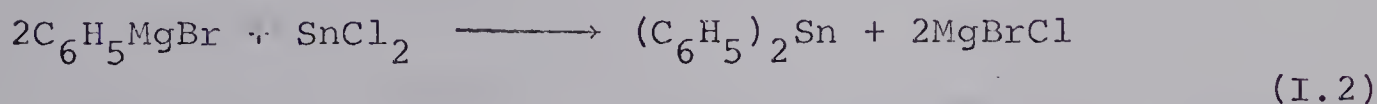
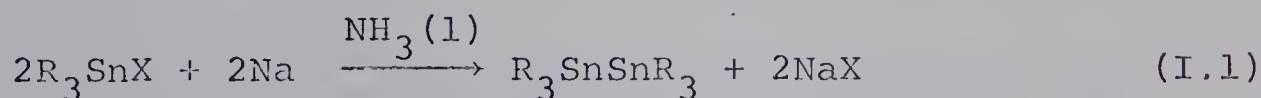
In the inorganic chemistry of tin the valence states of both two and four are well established. (Here, the term "valence" refers to the number of electrons used in bonding). However, in organotin chemistry, the lower valence state of two is ill-defined. Compounds of the general formula R_2Sn , for a long time considered to be Sn(II) species, are actually Sn(IV) compounds, since, upon preparation, they polymerize to form Sn-Sn bonds and tetravalent tin. Probably one of the most-studied members of this family is " $(C_6H_5)_2Sn$ ", first prepared by Böeseken and Rutgers (6) in 1923. The compound, however, was not well-characterized until recently. X-Ray studies by Olson and Rundle (7) showed that the compound (prepared by a method due to Kuivila and coworkers (8)) was hexameric, forming a chair-like structure (I) similar to that of cyclohexane.



I

Other R_2Sn units have also been shown to form catenation compounds with either cyclic or straight-chain structures (9).

Tin(IV) compounds in which this metal is bonded to itself or to other elements of Main group IV are well-known. As was mentioned earlier, compounds originally considered to be monomeric tin(III) derivatives are in fact dimeric, containing a tin-tin bond. They can be prepared by a Wurtz-type reaction (equation I.1) or by a disproportionation reaction using a tin(II) halide and Grignard reagent (equation I.2).



Hexaalkyl- and hexaarylditin compounds of the type R_3SnSnR_3 can be prepared by action of R_3SnM ($M = Li, Na, K$) on R_3SnX ($X = \text{halogen}$). This same procedure (equation I.3) can be used also to obtain mixed metal derivatives such as $(C_6H_5)_3Sn-Ge(C_6H_5)_3$ (10).



A number of well-characterized polytin compounds are now known. In addition to those investigated by Brown and Morgan (5) and Neumann and König (9), which have either cyclic or straight-chain structures, a compound having four $(C_6H_5)_3Sn$ groups bonded to a central tin atom is known (11).

The first report of a transition metal derivative of tin was made in 1942 by Hieber and Teller. (13) The characterization of the compound $Sn[Co(CO)_4]_2$, was difficult because of the lack of the physical techniques then available. Formulation of this compound thus rested entirely upon analysis.

Tin-transition metal chemistry has undergone very rapid expansion in the past six years. Compounds involving tin and sixteen transition group metals in various combinations have been synthesized to date. The following survey, necessarily abbreviated because of the considerable volume of literature available even now, has been designed to acquaint the reader with some of the background of this rapidly expanding field.

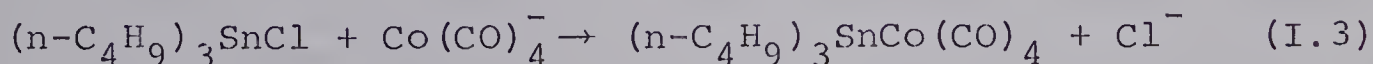
Almost all the work that has been reported involves the transition metal in a low oxidation state which appears to be a prerequisite for the formation of stable metal-metal bonds. Stabilization of the low oxidation state is obtained by use of π -acceptor ligands such as carbon

monoxide and various phosphines and arsines.

Table I lists representative compounds of all transition metals known at present to form direct bonds to tin. The majority of them were prepared by one of five basic methods. The method by which each was prepared is represented in the table by a letter A-E. The letter F represents reactions to which no general classification can be given. The following are brief discussions concerning each one.

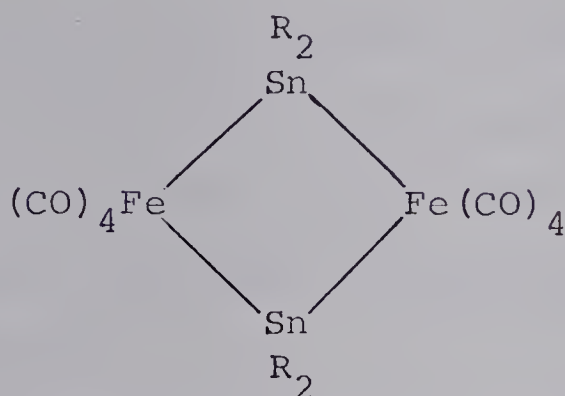
Method A - Metal Carbonyl Anions

The most widely-used method to date is one involving metathetical displacements of halogens by metal carbonyl anions. This procedure was first used by Hieber and Breu in 1956 (41) to prepare $\text{Co}(\text{CO})_4$ derivatives of tin (equation I.3) but did not come into prominence until



1962 when Gorsich (19) reported the first Mn-Sn derivatives prepared from $\text{NaMn}(\text{CO})_5$ and an organotin halide. In this case, the pentacarbonylmanganate (-I) anion was obtained by reaction of the dimeric carbonyl with sodium amalgam. Some novel systems have been obtained by this method. Patmore and Graham (30) described the preparation of the six-coordinate tin compound $(\text{acac})_2\text{Sn}[\text{Co}_2(\text{CO})_7]$ (acac =

acetylacetonate ion). Reaction of the dianion, $\text{Fe}(\text{CO})_4^{2-}$, by Sweet, et al. (42) with CH_3SnCl_3 gave a cluster compound formulated as $(\text{CH}_3)_4\text{Sn}_3\text{Fe}_4(\text{CO})_{16}$. Similar reactions using R_2SnCl_2 give structures (II) containing tin bridges.



II

Method B - Insertion Reactions

The term, "insertion reaction", in inorganic chemistry has recently been applied to reactions where a metal halide in a low valence state (e.g. $\text{Sn}(\text{II})$, $\text{In}(\text{I})$) will insert into a metal-metal bond increasing its oxidation state by two. It has been shown that for a reaction to proceed readily, there must be bridging carbonyls supporting the metal-metal bond as is the case in $\text{Co}_2(\text{CO})_8$.

The insertion into the Fe-Fe bond in $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ by SnCl_2 (equation I.4) was first reported by Bonati and Wilkinson (16). Patmore and Graham (43,44) have applied

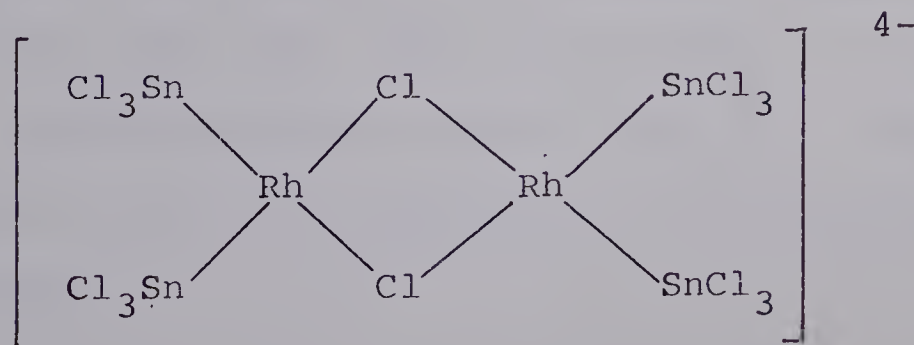
this procedure to a large number of compounds involving



not only SnCl_2 but also GeX_2 ($\text{X} = \text{halogen}$), InX , $\text{Ga}[\text{GaX}_4]$, and TlX .

The reaction is not limited to neutral metal carbonyl species. Ruff (45) reported the reaction of SnI_2 and GeI_2 with the anions $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ and $[\text{W}_2(\text{CO})_2]^{2-}$ to obtain products of the type $[(\text{CO})_5\text{MSnI}_2\text{M}(\text{CO})_5]^{2-}$ and $[(\text{CO})_5\text{MGeI}_2\text{M}(\text{CO})_5]^{2-}$.

It has been found that stannous halides will also insert into various transition metal-halogen bonds. Thus, the reaction of $(\text{Ph}_3\text{P})_2\text{PtCl}_2$ with SnCl_2 gives trans- $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PtCl}(\text{SnCl}_3)$ and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}(\text{SnCl}_3)_2$ (33,38). A number of polynuclear anionic species containing the SnCl_3 group have been prepared. Davies et al. (27) obtained the anion $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$ (III) by reaction of SnCl_2 with RhCl_3 .

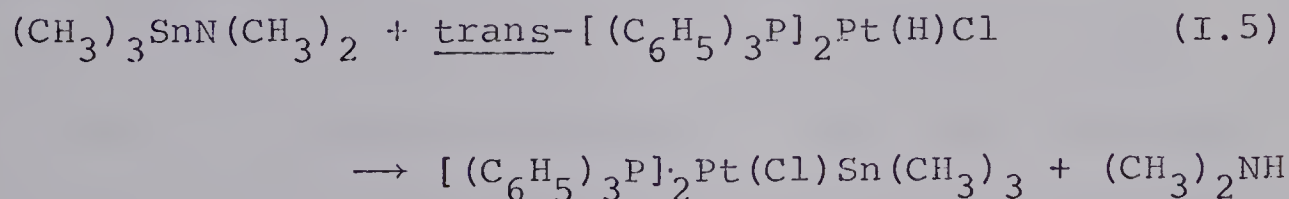


III

The mechanism of the insertion is not clearly understood, and whether the metal-halogen reactions and those of the metal-metal bonds involve similar intermediates is open to conjecture.

Method C - Elimination of a Neutral Molecule

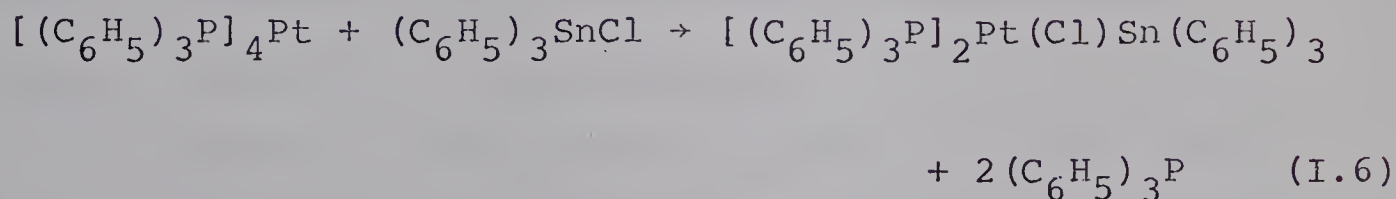
In a number of cases, reaction of two neutral species will result in the formation of a metal-metal bond and the elimination of another neutral species. Cardin and Lappert (46) found that combination of the reactive species $(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$ and a transition metal hydride (equation I.5) gave rise to an Sn-M compound and dimethylamine.



Recently, Kummer and Graham (18,47) have shown that reaction of Sn (IV) halides and organotin halides will result in an "oxidative elimination". For example, combination of $(\text{bipy})\text{Mo}(\text{CO})_4$ with SnX_4 , RSnX_3 and R_2SnX_2 (X = halogen) will give a seven-coordinate $(\text{bipy})\text{Mo}(\text{CO})_3\text{SnX}_3$, $-\text{SnX}_2\text{R}$ or $-\text{SnXR}_2$ species with the elimination of a molecule of carbon monoxide.

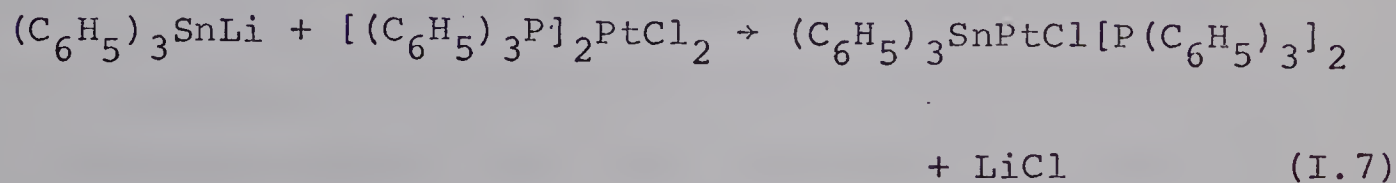
Method D - Oxidative-Addition Reactions

Oxidative-addition reactions have been found to occur with compounds of the platinum group metals where the metal is in a d^8 configuration coordinated by four or five ligands. For example, reaction of the Pt(0) compound $[(C_6H_5)_3P]_4Pt(0)$ with triphenyltin chloride (37) gives a Pt(II) compound (equation I.6).



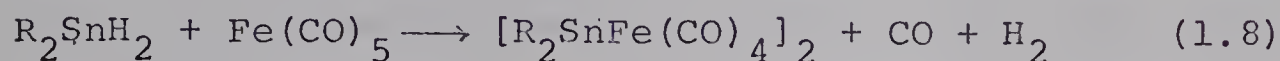
Method E - Halide Substitution by Lithium Derivatives

This method has been used to a very limited extent in palladium and platinum chemistry. Baird (36) obtained a monosubstituted Sn-Pt compound by reaction of $(C_6H_5)_3SnLi$ with cis $[(C_6H_5)_3P]_2PtCl_2$ as shown in equation I.7.



Besides the five methods outlined above, there are a number of other reactions (labelled F in Table I) which are not readily categorized. A large number of compounds have been obtained simply by mixing a metal carbonyl with

a tin halide. Patmore and Graham (28,29) reported the preparation of $\text{RSn}[\text{Co}(\text{CO})_4]_3$ and $\text{RXSn}[\text{Co}(\text{CO})_4]_2$ (R = alkyl, aryl) compounds by combination of cobalt carbonyl and either SnX_4 or RSnX_3 . Tetracarbonyliron dimers, $[\text{R}_2\text{SnFe}(\text{CO})_4]_2$, can be prepared by refluxing iron carbonyl with $\text{R}_2\text{Sn}(\text{CH}=\text{CH}_2)_2$ (R = butyl, methyl, ethyl) compounds with elimination of the vinyl groups (48). The same compounds have been obtained by J. D. Cotton et al. using R_2SnH_2 (equation 1.8) with iron pentacarbonyl (26).



Derivatives of compounds possessing Sn-metal bonds have also been obtained using these compounds as starting materials. For example, halogens and hydrogen halides can be used to replace organic groups with halogen atoms. Gorsich (19) obtained $\text{Cl}_3\text{SnFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ by cleavage of the phenyl groups on tin with hydrogen chloride. This fact alone is indicative of the great difference in metal-metal bond strengths of Sn-M compared to Sn-Sn. The latter can be cleaved easily by reaction with HX or X_2 (1).

Phosphine derivatives obtained using the Sn-M compound as starting material have been reported from a number of sources. Mono and bis-phosphine complexes of the types $(\text{CO})_4\text{Fe}(\text{MR}_2)_2\text{Fe}(\text{CO})_3\text{L}$ (L = phosphine or phosphite; M = Sn, Pb; R = alkyl or aryl) and $[\text{L}_2(\text{CO})_3\text{FeMR}_2]_2$ were reported by Kahn and Bigorgne (49). Diphosphine derivatives of $\text{R}_3\text{SnMn}(\text{CO})_5$ and $\text{X}_3\text{SnMn}(\text{CO})_5$ have been described by Bonati

and Ugo (20).

In spite of the large number of compounds known, only a few X-ray crystal structure determinations have been carried out. For the most part, metal-metal bonding has been inferred from method of synthesis, elemental analysis and infrared and nmr spectroscopic data.

The first X-ray structural analysis to be reported was of $(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$ (50), and it gave proof that the metal-metal bond did exist in this case. This and subsequent determinations on a number of compounds containing manganese or iron have indicated that the tin shows distorted tetrahedral bonding while the manganese or iron atoms show basic octahedral coordination.

One platinum complex for which X-ray data is available, the anion $[Pt(SnCl_3)_5]^{3-}$ has been shown to have a trigonal bipyramidal arrangement of tin atoms around the transition metal (51).

B. The Carbonyls of Manganese and Rhenium

Since these compounds are of great importance to the work presented in this Dissertation, a short description of their preparation and properties is appropriate at this point.

Although rhenium is the rarer of the two metals, its carbonyl $(Re_2(CO)_{10})$ has been known longer. It was first

synthesized in 1941 by Hieber and Fuchs (52) but because of the unavailability of spectroscopic tools any attempt at a structure assignment was speculative.

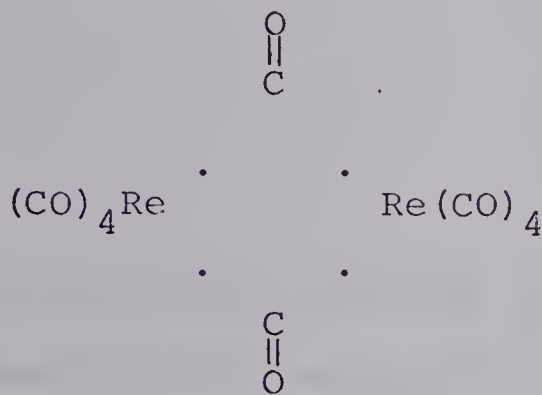
Manganese carbonyl, $\text{Mn}_2(\text{CO})_{10}$ was first reported in 1949 by Hurd and coworkers (53) by the reduction of MnI_2 with a Grignard under carbon monoxide pressure. Yields, apparently, were extremely low and the somewhat dubious characterization was made partly on the basis of qualitative tests for manganese in reaction solutions and washings and from a number of peaks found in the mass spectrum of an impure sample. Yields of a pure product of 1% were reported by Brimm, Lynch and Sesny (54) using MnI_2 under high pressure carbon monoxide with powdered copper and magnesium as reducing agents. These authors obtained an infrared spectrum and from it postulated the existence of a metal-metal bond.

A much improved method using anhydrous manganous acetate and triisobutylaluminum under carbon monoxide was reported in 1960 by Podall et al. (55). Yields of pure $\text{Mn}_2(\text{CO})_{10}$ above 70% are obtainable by this method.

Rhenium carbonyl is still obtained using the same basic procedure of Hieber and Fuchs (52). It is easily prepared (much more so than $\text{Mn}_2(\text{CO})_{10}$) by subjecting rhenium heptoxide to high pressure carbon monoxide. Yields of the white, highly stable crystalline material

can be almost quantitative.

The structures of both metal carbonyls are well established. Originally, the existence of a metal-metal covalent bond was so unprecedented that it was not seriously considered. Hieber and Fuchs (52) suggested that, for $\text{Re}_2(\text{CO})_{10}$, two $\text{Re}(\text{CO})_4$ units were connected via two bridging carbonyl groups (IV). However, this structure, in the light of infrared and magnetic data now available, can be ruled out. The effective atomic

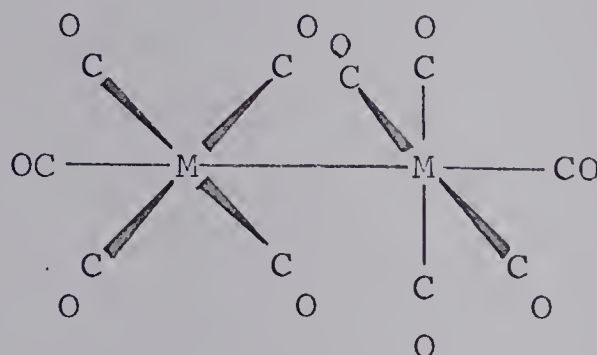


IV

number rule would require a metal-metal bond to account for the observed diamagnetism. Infrared measurements would show the absence of absorptions due to bridging carbonyl groups.

In 1956, using an erroneous infrared study, Cotton and coworkers (56) postulated a structure which did not invoke a metal-metal bond and, in fact, a bond of this type was ruled out on the basis of the data.

X-Ray structural analysis by Dahl, Ishishi and Rundle (57) in 1957 finally settled the controversy for both metal carbonyls. It was shown that there were indeed direct metal-metal bonds by which two $M(CO)_5$ units were connected (V). This was the first physical proof that



V

a covalent, electron pair bond between transition metals did exist and showed that the molecules possessed D_{4d} symmetry with each $M(CO)_5$ group turned 45° with respect to the other. The metal-metal bonds were longer ($\sim 0.5\text{\AA}$) than those that would be expected from the sum of normal covalent radii, with Mn-Mn distance of 2.93\AA and one for the Re-Re bond of 3.02\AA .

Manganese carbonyl has received most attention as far as chemical studies are concerned, as a result of its greater availability and lower cost. From the standpoint of this Dissertation, the most important reaction of

these carbonyls is that of cleavage of the metal-metal bond by sodium to form the $[M(CO)_5]^-$ species. This will be discussed in the following chapter.

TABLE I
EXAMPLES OF KNOWN COMPOUNDS CONTAINING
TIN-TRANSITION METAL BONDS^a

Transition Metal	Compound	Synthetic Method ^c	Ref.
Cr	$\text{Ph}_3\text{SnCr}(\text{CO})_3\text{Cp}^b$	A	14, 15
Mo	$\text{Me}_3\text{SnMo}(\text{CO})_3\text{Cp}$	A	14
	$\text{Cl}_2\text{Sn}[\text{Mo}(\text{CO})_3\text{Cp}]_2$	B	16
	$[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$	A, B	17
	$\text{bipy}(\text{CO})_3\text{ClMoSnCl}_3^b$	C	18
	$\underline{\text{o}}\text{-phen}(\text{CO})_3\text{ClMoSnMeCl}_2^b$	A	15
W	$\text{Ph}_2\text{Sn}[\text{W}(\text{CO})_3\text{Cp}]_2$	A	15
	$\text{Cl}_3\text{SnW}(\text{CO})_3\text{Cp}$	B	16
	$\text{bipy}(\text{CO})_3\text{IWSnMeI}_2$	C	18
	$\underline{\text{o}}\text{-phen}(\text{CO})_3\text{ClWSnEtCl}_2$	C	18
Mn	$\text{Ph}_3\text{SnMn}(\text{CO})_5$	A	19
	$\text{Ph}_3\text{SnMn}(\text{CO})_4\text{PPh}_3$	A	19
	$\text{Br}_3\text{SnMn}(\text{CO})_3(\text{diphos})^b$	-	20
	$\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5][\text{Re}(\text{CO})_5]$	A	21
Re	$\text{Ph}_3\text{SnRe}(\text{CO})_5$	A	22
	$\text{BrSn}[\text{Re}(\text{CO})_5]_3$	A	22
Fe	$(\text{Ph}_3\text{Sn})_2\text{Fe}(\text{CO})_4$	A	23, 24
	$[\text{Me}_2\text{SnFe}(\text{CO})_4]_2$	A, F	25, 26, 48

TABLE I (continued)

Transition Metal	Compound	Synthetic Method ^C	Ref.
	$\text{Sn}[\text{Fe}(\text{CO})_4]_4$	F	26
	$\text{Et}_4\text{Sn}_3[\text{Fe}(\text{CO})_4]_4$	F	26
	$\text{Me}_3\text{SnFe}(\text{CO})_2\text{Cp}$	A	14
	$\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$	B	16
Ru	$[\text{Et}_4\text{N}]_2[\text{Ru}(\text{SnCl}_3)\text{Cl}_2]$	B	27
	$(\text{Ph}_3\text{Sn})_2\text{Ru}(\text{CO})_4$	A	34
Co	$\text{Ph}_3\text{SnCo}(\text{CO})_4$	A	24, 43
	$\text{Br}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	B	28
	$n\text{-BuSn}[\text{Co}(\text{CO})_4]_3$	F	29
	$(\text{Acac})_2\text{Sn}[\text{Co}_2(\text{CO})_7]_b$	A	30
	$\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_3\text{P}(n\text{-Bu})_3]_2$	B	31
Rh	$\text{Me}_3\text{SnRh}(\text{CO})_2\text{PPh}_3)_2$	A	32
	$(\text{Ph}_3\text{P})_3\text{RhSnCl}_3$	B	33
	$[\text{Me}_4\text{N}]_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$	B	27, 33
Ni	$\text{Cl}_2\text{Sn}[\text{Ni}(\text{CO})\text{Cp}]_2$	B	28
Pd	$[\text{Ph}_4\text{As}]_2[\text{PdCl}(\text{SnCl}_3)_2]$	B	35
Pt	$(\text{Ph}_3\text{P})_2\text{PtCl}(\text{SnPh}_3)$	D, E	36, 37
	$(\text{Ph}_3\text{P})_2\text{Pt}(\text{SnCl}_3)_2$	B	38
	$[\text{Me}_4\text{N}]_4[\text{Pt}_3\text{Sn}_8\text{Cl}_{20}]$	B	39
	$(\text{Ph}_3\text{P})_2\text{PtCl}(\text{SnMe}_3)$	C	46
Cu	$(\text{Ph}_3\text{P})_3\text{CuSnCl}_3$	B	40

TABLE I (continued)

Transition Metal	Compound	Synthetic Method ^c	Ref.
Ag	$(\text{Ph}_3\text{P})_3\text{AgSnCl}_3$	B	40
Au	$(\text{Ph}_3\text{P})_3\text{AuSnCl}_3$	B	40

-
- a. This table excludes compounds synthesized for the first time in this work.
- b. In a number of tables in this Dissertation, organic groups and ligands are represented by letter symbols as follows: Ph = C_6H_5 ; Me = CH_3 ; n-Bu = $\text{n-C}_4\text{H}_9$; Et = C_2H_5 ; Vi = $\text{CH}_2=\text{CH}$; Cp = π -bonded cyclopentadienyl; bipy = 2,2'-bipyridyl; o-phen = ortho-phenanthroline; diphos = 1,2-bis(diphenylphosphino)-ethane, Acac = acetylacetonate.
- c. See Text.

CHAPTER II

MONO (PENTACARBONYLMANGANESE-AND RHENIUM) DERIVATIVES

The first report of organic compounds of Main Group IV metals bonded to manganese carbonyl was made by R. D. Gorsich (19) in 1962. Compounds of the type $R_{3-n}X_n \text{SnMn(CO)}_5$ ($R = \text{aryl}$; $X = \text{Cl, Br}$; $n=0,1,2,3$) were prepared and some of their properties discussed.

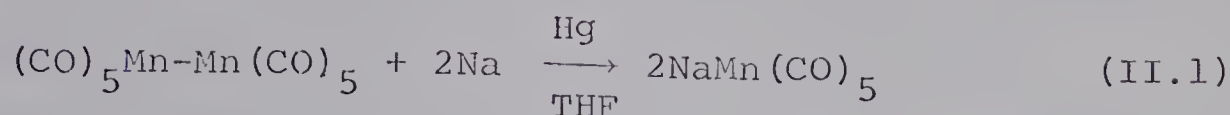
While the present work was in progress, Nesmeyanov and coworkers (22) published a brief report of some rhenium compounds analogous to those of Gorsich.

In this chapter, preparation of new related species containing manganese and rhenium carbonyl groups as well as a reinvestigation of the previous work for the purpose of obtaining infrared data will be discussed. Spectroscopic studies are discussed in Chapters VII and VIII.

Anion Reactions

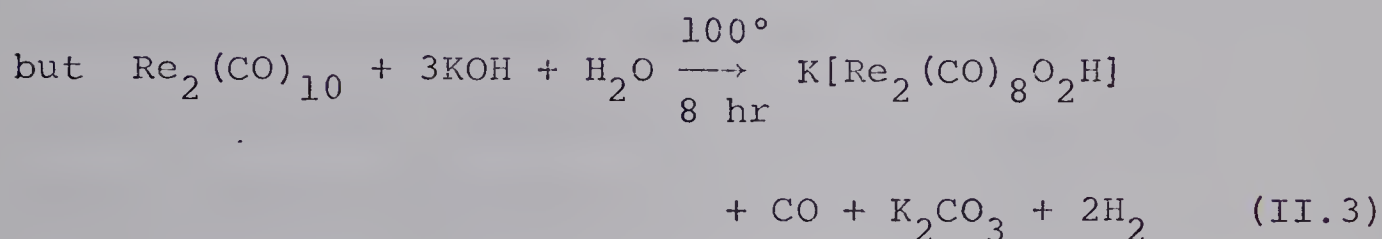
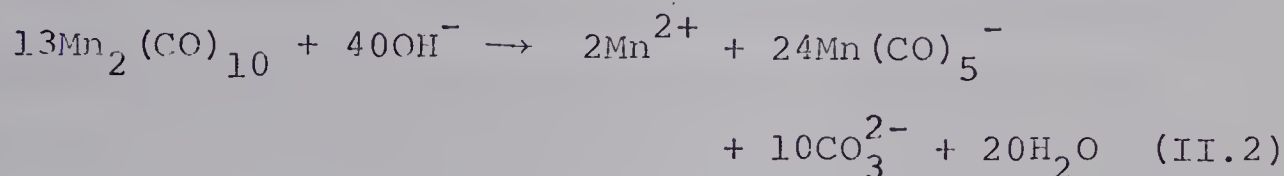
The use of metal carbonyl anions as reactive intermediates has found very wide acceptance in organometallic chemistry in the last ten years. Pioneering work in this field was done in Germany by Hieber and coworkers who first prepared NaMn(CO)_5 in 1957 by reaction of 1% sodium amalgam with $\text{Mn}_2(\text{CO})_{10}$ in tetrahydrofuran (THF)

solution:



However, preparation of the anion need not be limited to use of sodium as the reducing agent or to THF as solvent. Lithium and diethyl ether, for example, provide satisfactory alternatives.

Hieber and Wagner (58) found also that $\text{Mn}(\text{CO})_5^-$ (but not $\text{Re}(\text{CO})_5^-$) could be made using strong base in aqueous solution:



Reaction II.2 is a convenient method of obtaining the anion but suffers from two disadvantages. One drawback is that about 7% of the manganese of the $\text{Mn}_2(\text{CO})_{10}$ is lost as Mn^{2+} . The second disadvantage, more important from the viewpoint of this work, is that the strongly basic solution would react with the organotin halides.

However, the use of an amalgam is probably the

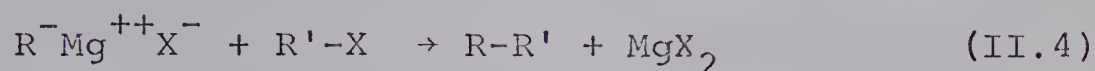
generally accepted method. King (59) points out in a review of alkali metal derivatives of metal carbonyls that mercury may act as a catalyst in the cleavage reaction by forming an intermediate of the type Mn-Hg-Mn or Re-Hg-Re . It is known (60) that mercury does react with $\text{Co}_2(\text{CO})_8$ to give $\text{Hg} [\text{Co}(\text{CO})_4]_2$ but in the cases of rhenium or manganese no species of this type were observed in the present work.

The sodium salts of both manganese and rhenium carbonyl may be isolated as highly air-sensitive powders from tetrahydrofuran (58,61). Sodium pentacarbonylmanganese is almost colorless whereas the rhenium analog is yellow and contains half a mole of solvent. Generally the salts are not isolated but used in the reaction solution. Hieber (58) reported that solutions of $\text{NaMn}(\text{CO})_5$ were nearly colorless. However this writer's experience with it showed solutions to be, without exception, a dull green color. This could possibly be due to differences in concentration: i.e., in the amount of solvent used.

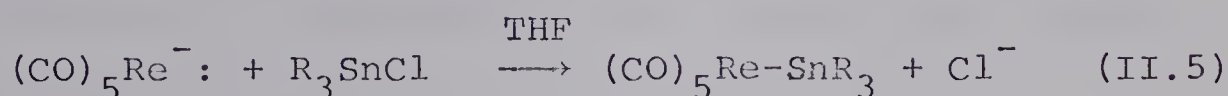
On the other hand, $\text{NaRe}(\text{CO})_5$ was found in the present work to form blood-red solutions. This is in agreement with the earlier reports. (61) This coloration has been attributed to formation of polynuclear carbonyl-metallates such as $\text{Re}_4(\text{CO})_{16}^{2-}$. (62) Formation of such species in preparation of $\text{NaRe}(\text{CO})_5$ could serve to lower yield of the latter.

Anion Reactions with Organotin Halides

In discussing the type of reaction that occurs between a metal carbonyl anion, say $\text{Re}(\text{CO})_5^-$, and an organotin halide $\text{R}_{4-n}\text{SnCl}_n$ ($n=1,2,3$) analogy can be made with that of the familiar Grignard reagent in organic chemistry. In this case a nucleophilic attack by the Grignard upon some species $\text{R}'\text{-X}$ occurs:

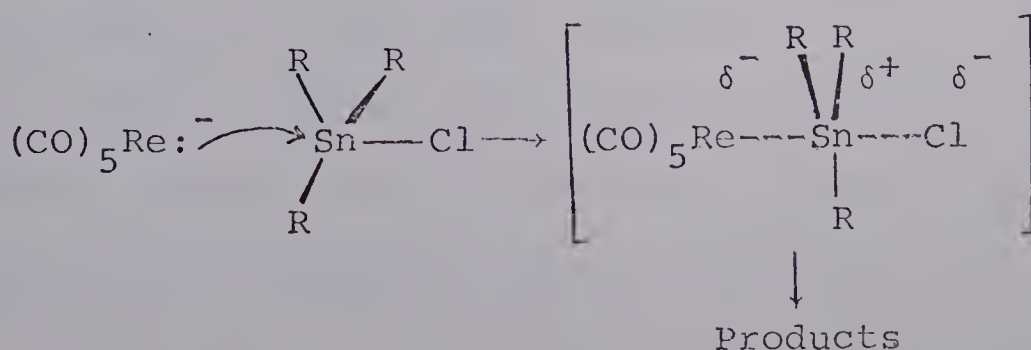


In the halo-tin reaction, nucleophilic attack by the metal carbonyl anion upon the tin (or any other main group IV metal) can be assumed to occur:



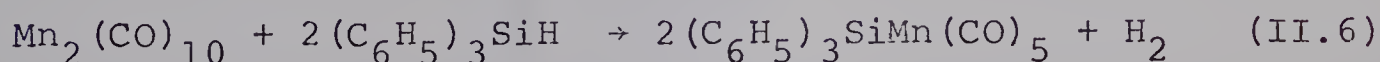
(R = alkyl or aryl)

The mechanism of this reaction is a matter for speculation. It could be considered to be an $\text{S}_{\text{N}}2$ reaction in which an intermediate 5-coordinate tin transition state occurs:



However, we cannot rule out the possibility of an S_N1 -like reaction in which the organotin halide undergoes dissociation prior to attack by the anion. No kinetic studies have been published to date and probably studies of these reactions would prove to be most difficult owing to the speed with which they occur.

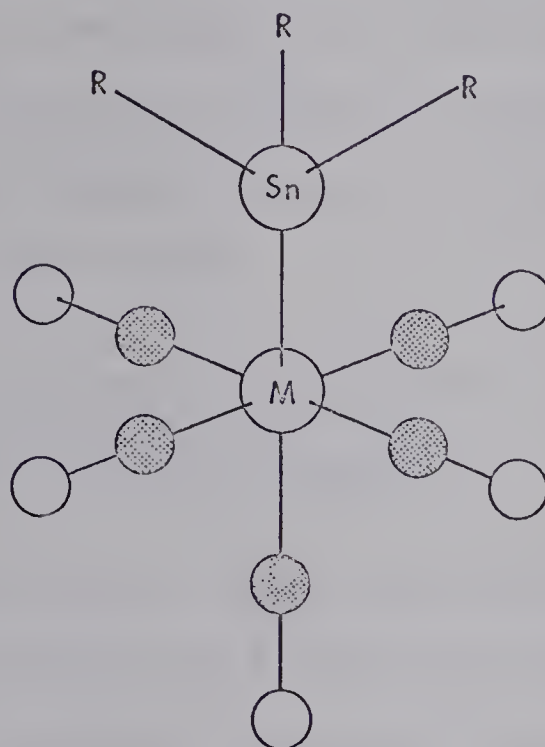
It is interesting to note that $(C_6H_5)_3SiCl$ does not react with $NaM(CO)_5$ as would be expected. Gorsich(19) reported the formation of a dark red, unstable material which he assumed was $(C_6H_5)_3SiMn(CO)_5$. However, more recent studies have shown that this is not the case (63). By reacting triphenylsilane $(C_6H_5)_3SiH$ with $Mn_2(CO)_{10}$ (or $Re_2(CO)_{10}$) white crystalline solids were obtained with stabilities comparable to the heavier metal analogs of Ge, Sn and Pb.



Structural Studies

X-Ray crystal structures of $(C_6H_5)_3SnMn(CO)_5$ and $(CH_3)_3SnMn(CO)_5$ have been reported by R. F. Bryan and H. P. Weber (67,68). The studies showed that the tin atoms exhibited basic tetrahedral coordination and, as expected the manganese was hexacoordinate (VI). However in

both cases the organic groups on tin were slightly displaced from idealized tetrahedral positions. The C-Sn-C angle in $(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$ is 107.4° while in the triphenyl analog the angle was reduced to 106.0° .



○ OXYGEN
● CARBON
M = Mn, Re

VI

Of particular note is the fact that no difference in the Sn-Mn bond lengths in the two compounds was found, both having a value of 2.674\AA . The related compound $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ (19) has been studied by Bryan (50) also and found to have a metal-metal

distance of 2.627^oÅ. This indicates that bond distances are sensitive to ligands attached to the transition metal. It is to be expected that the same effect would be observed for a change of ligands on tin although none was found for the two compounds $(\text{CH}_3)_3\text{Sn}-$ and $(\text{C}_6\text{H}_5)_3-\text{SnMn}(\text{CO})_5$ where the ligands are very similar.

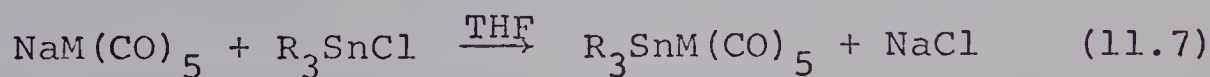
The effect on bond lengths of placing one and two additional metal carbonyl groups on the tin will be discussed in the next chapter.

RESULTS AND DISCUSSION

a. Compounds of the Type $\text{R}_3\text{SnM}(\text{CO})_5$

As was mentioned at the beginning of the chapter, Gorsich (19) prepared the first known organo- and halotin derivatives of manganese carbonyl. Accordingly it was the intention of this present work to extend studies to rhenium carbonyl and to expand the preparation of $\text{Mn}(\text{CO})_5$ derivatives for the purpose of infrared investigations.

Reactions (eq. 11.7) between $(\text{CO})_5\text{M}^-$ ($\text{M} = \text{Mn}, \text{Re}$)



and the monohalides R_3SnCl ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) are quite similar and were handled accordingly. After the THF

solution of the sodium salt was prepared, the amalgam was removed and the crystalline organotin halide added as a solid. Reaction, as noted by a change in color of the mixture, was almost immediate and precipitation of NaCl was observed.

Work-up of the reaction mixtures was accomplished either by complete removal of solvent and subsequent extraction with hexane, or by concentrating the THF solution and pouring it over ice-water. In the case of the phenyl derivatives this procedure led to higher yields. The higher yields could be attributed to the fact that these compounds are quite hydrophobic in nature.

Recrystallization of $(C_6H_5)_3SnRe(CO)_5$ was done in hexane whereas $(CH_3)_3SnRe(CO)_5$, which was much more soluble, could only be obtained from a petroleum ether solution cooled to -78° . Like their $Mn(CO)_5$ analogs (19,64) the rhenium derivatives of $(C_6H_5)_3Sn-$, $(C_6H_5)_3Ge-$ and $(C_6H_5)_3Pb$ are crystalline solids ranging from white to pale yellow. All the rhenium compounds had slightly lower melting points. In solution all are stable for varying lengths of time but do decompose slowly on exposure to light.

A somewhat larger difference in properties was exhibited by $(CH_3)_3SnRe(CO)_5$ when compared with

$(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$. The latter compound was prepared in this laboratory by P. B. Simons. (63) It was found to be a liquid at room temperature and required sublimation at 0° onto a -78° cold finger to obtain crystals. The rhenium analog, also a white crystalline solid, had a melting point some 30° higher and could be sublimed in high vacuum at room temperature. By contrast the phenyl derivatives were much less volatile.

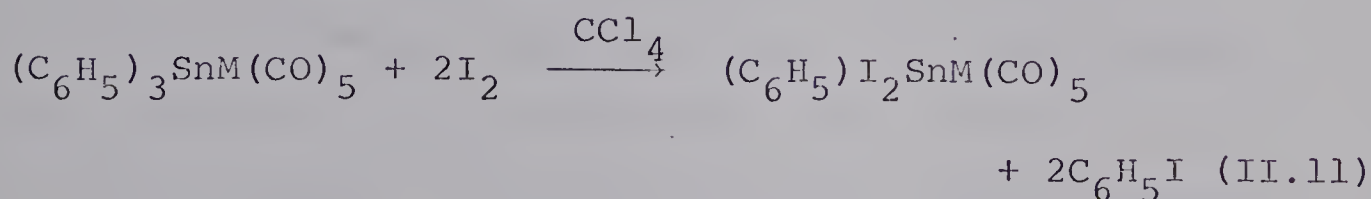
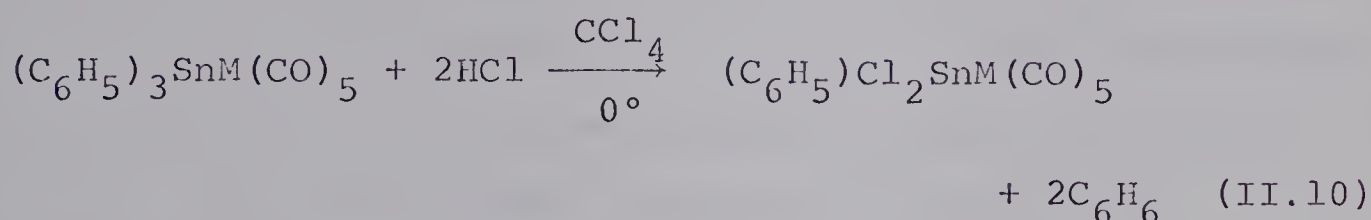
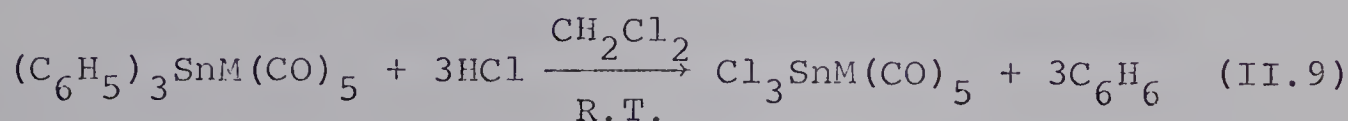
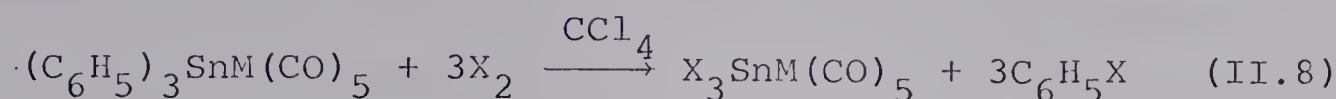
Solubilities of the rhenium carbonyl compounds are very similar to those of manganese. They are only moderately soluble in straight-chain hydrocarbon solvents such as pentane or hexane but quite soluble in more polar solvents; for example, methylene chloride, alcohol, and acetone.

Thermal stabilities of the trialkyl- and aryl compounds are good. All have sharp melting points and do not decompose at even higher temperatures. For example, Gorsich (19) observed that $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ only began to evolve carbon monoxide at 195° . Similar or higher stabilities of the rhenium analogs were noted in the present work.

b. Compounds of the Type $\text{R}_{3-n}\text{X}_n\text{SnM}(\text{CO})_5$

Compounds of the type $\text{R}_{3-n}\text{X}_n\text{SnM}(\text{CO})_5$ ($\text{R}=\text{CH}_3$, C_6H_5 ;

X = Cl, Br, I; n = 1, 2, 3) were obtainable by several synthetic routes. The most widely used of these routes is the cleavage reaction represented in the four equations below:



The method used by Gorsich (19) to prepare Cl_3Sn and Br_3Sn species is given by equation II.8. Similar procedures were used initially in this work to prepare the corresponding rhenium compounds; however in later preparations of $Cl_3SnMn(CO)_5$ and $Cl_3SnRe(CO)_5$ anhydrous hydrogen chloride (eq. II.9) was found to be a superior reagent. Use of the elemental halogen in the case of Cl_2 or Br_2 resulted in the desired product plus small amounts of the metal pentacarbonyl halide, e.g. $Mn(CO)_5Br$. Hydrogen chloride did have the advantage of greater selectivity due to its lower reactivity. Consequently none of the products due

to metal-metal bond cleavage were detected. Also, the by-product of equation II.8, benzene, would be somewhat easier to remove from the reaction mixture than the phenyl halide. Both methods for obtaining $\text{Cl}_3\text{SnRe}(\text{CO})_5$ were reported by Nesmeyanov et al. (22) who found that use of HCl improved yields by about 5%.

Thus, the trichlorides were obtained preferably using anhydrous HCl which was bubbled through solutions of the $(\text{C}_6\text{H}_5)_3\text{Sn}$ - derivatives in CH_2Cl_2 at room temperature. The bromides and iodides were prepared using the halogen in CCl_4 . For the iodides, reactivity of iodine was such that stirring of $(\text{C}_6\text{H}_5)_3\text{SnM}(\text{CO})_5$ with three moles of the halogen at room temperature- gave mixtures of the di- and triiodides. To obtain only the latter compound excess I_2 in refluxing solvent was necessary.

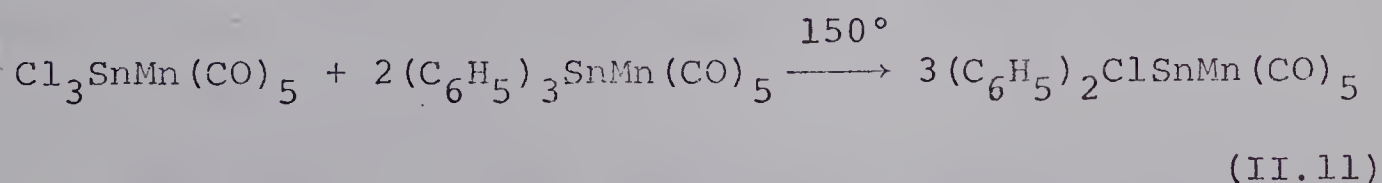
In this present work $(\text{C}_6\text{H}_5)\text{Cl}_2\text{Sn}$ - and $(\text{C}_6\text{H}_5)\text{I}_2\text{SnRe}(\text{CO})_5$ were prepared for the first time. The former compound was obtained according to equation II.10 in which anhydrous HCl was bubbled into a solution of the triphenyl derivative in CCl_4 . As for the manganese analog, it was necessary to carry out the reaction in the cold to prevent too great a formation of the trichloride. A slight precipitate of the latter compound provided a convenient indication of when to terminate addition of HCl.

The iodides, $(\text{C}_6\text{H}_5)\text{I}_2\text{SnM}(\text{CO})_5$, were easily prepared

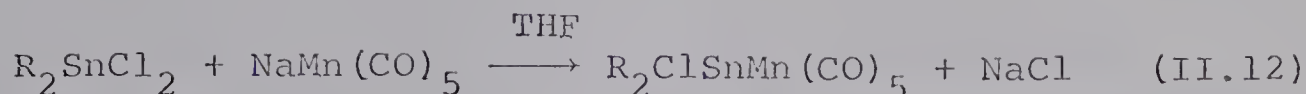
by reaction of the triphenyltin compounds with a slight excess of the element at room temperatures, reaction completion being indicated by discharge of the deep color of iodine. $(C_6H_5)_3Br_2SnRe(CO)_5$ (22) and the manganese analog (19) were formed using similar reactions with bromine.

Only phenyldihalotin species can be prepared easily. Attempts in this laboratory to prepare $(CH_3)_2Cl_2SnMn(CO)_5$ in even low yields failed. H. C. Clark (66) reported its formation by heating $(CH_3)_3SnMn(CO)_5$ with 2 moles of anhydrous HCl in pentane in a Carius tube for one week at 60°. Yield of the product was 26%. Some $(CH_3)_2ClSnMn(CO)_5$ was also obtained.

It is with the compounds $R_2XSnM(CO)_5$ that a major difference in case of preparation is noted. Gorsich (19) used the well-known 'Kocheshkov' or redistribution reaction (65) of organotin chemistry to obtain $(C_6H_5)_2ClSnMn(CO)_5$.



This reaction was repeated in the present work and, indeed, the desired compound was obtained but only after it was separated from impurities on a chromatographic column. To overcome this handicap an improved method as shown in equation II.12 was used. This method was actually an



extension of one first used by W. A. G. Graham (69) to prepare the dimethyl derivative. Reaction of $(\text{CH}_3)_2\text{SnCl}_2$ or $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ with an equimolar amount of the anion will give mainly $\text{R}_2\text{Sn}[\text{Mn(CO)}_5]_2$ (see Ch. III) if the reaction mixture is worked up within an hour of addition. However, stirring of the mixture overnight (or for 15-24 hr.) will result in $\text{R}_2\text{ClSnMn(CO)}_5$ as the only or major product. In effect, then, a 'Kocheshkov' type reaction is occurring in solution between the bis-metal carbonyl species and excess R_2SnCl_2 :



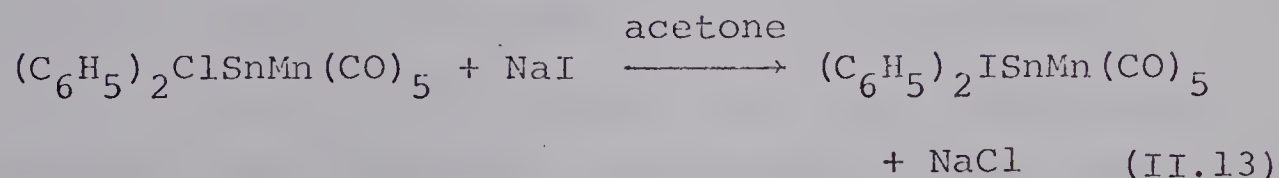
The reaction involves an exchange between two tin atoms of chlorine and an Mn(CO)_5 group. The mechanism of this reaction is not known and represents a large area for future investigation.

Application of this reaction to rhenium was not as fruitful. Stirring equimolar amounts of NaRe(CO)_5 and $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ for twenty-three hours gave the bis compound $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{Re(CO)}_5]_2$ as major product. The reaction with $(\text{CH}_3)_2\text{SnCl}_2$ was equally disappointing. After a reaction period of about an hour, an infrared spectrum of the

mixture showed at least twelve bands in the terminal carbonyl stretching region. After 18 hours the spectrum had not changed indicating that there was a very complex mixture present. Attempts at separating the mixture were only slightly profitable. An nmr spectrum indicated at least five methyltin species were present even after partial separation. This is clearly not a satisfactory preparative method.

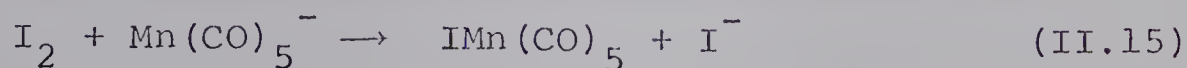
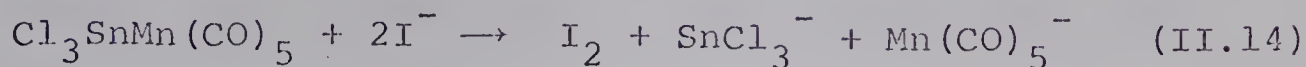
However, $(\text{C}_6\text{H}_5)_2\text{ClSnRe}(\text{CO})_5$ was obtained using the 'Kocheshkov' method. (65) As with the previous case with manganese, the product was contaminated with some of the triphenyltin starting material but was fortunately more easily purified.

The monoiodide $(\text{C}_6\text{H}_5)_2\text{ISnMn}(\text{CO})_5$ was easily obtained by a metathetical reaction (equation II.13) which involved reaction of the chloride with excess sodium iodide in acetone.



Use of the metathetical displacement reaction to obtain the triiodide provided some interesting results. Reaction of $\text{Cl}_3\text{SnMn}(\text{CO})_5$ with NaI in acetone produced an immediate dark red color which appeared to be free iodine. Work-up

of the mixture gave $\text{I}_3\text{SnMn}(\text{CO})_5$ as the major product but also, surprisingly the known compound $\text{IMn}(\text{CO})_5$ (54). The oxidation-reduction process which is evidently a side-reaction might therefore be written speculatively as



A similar reaction was found to occur between I^- and SnCl_4 in acetone to give a deposit of SnCl_2 . This is interesting since in aqueous solution, classical redox potential considerations allow reduction of stannous ion by iodine but not the reverse.

All the halotin derivatives in the solid state are stable to light and air with the exception of the tri-iodides which do darken slightly over a period of weeks if exposed to light. In solution they are stable for long periods if kept in the dark. Photodecomposition does occur slowly with the iodides being most susceptible. The trichloro- and tribromotin derivatives of both metal carbonyls are the most stable members of the series. They do not melt usually but decompose at temperatures from 168° to in excess of 250° .

Colors of the solid compounds range from white to bright yellow. In any given series colors range from

white for the chlorides through to yellow for the more highly substituted iodides.

All but the trichloro- and tribromo species are moderately soluble in hydrocarbon solvents. To obtain nicely crystalline samples of the trichloro- and tribromo derivatives, the solvent pair of CH_2Cl_2 -petroleum ether was used. All the halo derivatives are highly soluble in more polar solvents. In acetone or alcohol the trihalides are hydrolyzed by water to form insoluble white solids. (19)

c. Reactivity of the Metal-Metal Bond

The preparations of the halogenated compounds where the halogen or a hydrogen halide are used exhibit the remarkable inertness possessed by the Sn-M bond. As has been seen, reaction of the triphenyltin derivatives with Cl_2 , Br_2 or I_2 gave as main products ones in which the carbon-tin bonds and not the metal-tin bonds were cleaved. For Br_2 and I_2 even at elevated temperatures in CCl_4 no $\text{XM}(\text{CO})_5$ was isolated. Anhydrous hydrogen chloride was even more selective as was also found in the case of the bis-metal carbonyl compounds discussed in Chapter III.

Metal-tin bonds exhibit what one might consider to be ideal intermediate reactivity when compared with other main group IV metals. Gorsich(19) found that at 25° ,

$(C_6H_5)_3PbMn(CO)_5$ reacted with hydrogen chloride to give $ClMn(CO)_5$ and an unidentified inorganic lead species.

Reaction of $(C_2H_5)_2Pb[Mn(CO)_5]_2$ gave $ClMn(CO)_5$ and organolead halides. Thus it would seem that metal-Pb bonds are less inert and more susceptible to cleavage.

On the other hand, germanium-manganese and germanium-rhenium bonds have been shown by Nesmeyanov (21,70) et al. to have increased resistance to cleavage by halogens or hydrogen halides. Indeed, the phenylgermanium derivatives show increased resistance to carbon-Ge cleavage. Reaction in boiling solvent over periods of hours was required to obtain the trihalo compounds. The diphenyl- (monohalo) germanium compounds were easily obtained at room temperature using X_2 or HX . Similar attempts with C_6H_5-Sn systems resulted only in inseparable mixtures.

EXPERIMENTAL SECTION

Melting points were determined using a Kofler Hot Stage mounted on an Olympus binocular microscope.

Analyses were performed by the Microanalytical Laboratory of this department, by Alfred Bernhardt Mikroanalytisches Laboratorium, Mulheim, West Germany and by Pascher Mikroanalytisches Laboratorium, Bonn, West Germany.

Molecular weights were obtained using a Mechrolab

Osmometer in this department. Exact masses were determined using an AEI double focusing mass spectrometer operating at 1.5 to 2.2 kv.

Reactions were carried out using a static nitrogen atmosphere. Commonly used standard-taper glassware was employed in all reactions.

The starting materials $(C_6H_5)_3SnCl$, $(CH_3)_3SnCl$, $(C_6H_5)_2SnCl_2$ and $(CH_3)_2SnCl_2$ were obtained commercially from M & T Chemicals Inc., Rahway, N. J. Triphenylbromogermane was prepared by reaction of HBr with tetraphenylgermane in chloroform (71). Triphenyllead chloride was obtained by reaction of tetraphenyllead with HCl.

Solvents

Tetrahydrofuran (THF): This cyclic ether was stored over either sodium wire or sodium-lead alloy. Immediately before use it was distilled from lithium aluminum hydride using a 14 inch Vigreux fractionating column.

Solvents used for recrystallizations were obtained commercially and used without further purification. Petroleum ether refers to hydrocarbon solvent with a 30°-60° boiling range. Ligroin refers to a hydrocarbon solvent, boiling range 80°-100°.

Preparation of Sodium Pentacarbonylmanganese ($Na^+Mn(CO)_5^-$) and Sodium Pentacarbonylrhenium ($Na^+Re(CO)_5^-$): The starting compounds, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, were obtained as

as described in Chapter I. Preparation of the $\text{Na}^+\text{Mn}(\text{CO})_5^-$ was carried out using a procedure based on the one given by Gorsich (19). $\text{Na}^+\text{Re}(\text{CO})_5^-$ was prepared in a similar fashion.

Apparatus consisted of a 3-neck round-bottom flask having either a small indentation of about 0.5 cm in depth or a side-arm fitted with a stopcock. These modifications enabled a more facile removal of sodium amalgam at the completion of the reaction.

Sodium amalgam was prepared at approximately 1% concentration by addition of freshly cut sodium pieces to triple-distilled mercury under a stream of nitrogen. Because of the vigorous nature of the reaction addition was carried out slowly. The dry THF would not be added until the amalgam cooled.

In a typical reaction, 30 ml. of THF was used with Na/Hg prepared from 4 ml. (54.4 g.) of mercury and 0.5 g of sodium. To this mixture (stirred magnetically) was added 3 gm (0.26 mmole) of $\text{Mn}_2(\text{CO})_{10}$. Reaction was immediate and after 1 hr., a green mixture was obtained. (in the case of $\text{NaRe}(\text{CO})_5^-$ the solution became blood red) Amalgam was removed by use of a 10 c.c. syringe fitted with a 5 inch needle. The solution was generally washed with one or two ml. of fresh mercury before the next reaction step.

The following procedures are given for compounds which are new or had not been reported at the time the work was begun or for which improved methods have been found.

Triphenyl(pentacarbonylrhenium)tin(IV); $(C_6H_5)_3SnRe(CO)_5$:

Rhenium carbonyl (1 g., 1.5 mmoles) in 30 ml. of THF was stirred over 4 ml of 1% sodium amalgam for 1 hour under nitrogen. After removal of the amalgam, $(C_6H_5)_3SnCl$ (1.1 g., 2.8 mmoles) was added and the mixture stirred for $1\frac{1}{2}$ hr. During this time the mixture became yellow-green in color. After partial removal of solvent at reduced pressure (Buchi 'Rotavapor') the mixture was poured over ice-water to precipitate the product which was filtered on a Büchner funnel after standing for a few minutes. The crude product was dried in a vacuum desiccator over 'Drierite'. Crystallization from hexane afforded white plates (60% yield). Subsequent preparations on larger scales provided yields as high as 80% based on the $Re_2(CO)_{10}$.

Triphenyl(pentacarbonylrhenium)germanium(IV), $(C_6H_5)_3GeRe(CO)_5$:

To a solution of $NaRe(CO)_5$ (3 mmoles) in 20 ml THF prepared as above was added $(C_6H_5)_3GeBr$ (1.18 g, 3.1 mmoles) and the mixture stirred for $\frac{1}{2}$ hour. After filtration to remove NaBr, the solution was evaporated to dryness at

reduced pressure and recrystallized from n-hexane to give white crystals yield 0.58 g. (30%).

Triphenyl(pentacarbonylrhenium)lead(IV), $(C_6H_5)_3PbRe(CO)_5$:

To a THF solution (30 ml) of $NaRe(CO)_5$ prepared from 1 g of $Re_2(CO)_{10}$ was added Ph_3PbCl (1.45 g , 3 mmoles) and the mixture stirred for 15 min. The mixture was filtered and solvent was removed at the rotary evaporator to give a red oil which slowly crystallized. Extraction with n-hexane gave a yellow solution which afforded a yellow solid on cooling. Recrystallization from petroleum ether (30°-60°) gave pale yellow crystals.

Trimethyl(pentacarbonylrhenium)tin(IV), $(CH_3)_3SnRe(CO)_5$:

To a solution of $NaRe(CO)_5$, prepared as above, was added $(CH_3)_3SnCl$ (0.6 g , 3 mmoles) and the mixture stirred for 15 min. After filtration, it was concentrated to 2-3 ml and petroleum ether (~10 ml) added. A small amount of curdy, green solid which formed was filtered off and the solution concentrated to $\frac{1}{2}$ the volume. Cooling to -78° afforded pale yellow crystals which were sublimed in vacuo to give a white product in somewhat low yield.

Trichloro(pentacarbonylrhenium(tin(IV); $Cl_3SnRe(CO)_5$:

Excess chlorine was passed through a solution of $(C_6H_5)_3SnRe(CO)_5$ (2 g , 3 mmoles) in 25 ml CCl_4 at

room temperature until a white precipitate formed. The precipitate was filtered off and washed with petroleum ether. Dissolution in methylene chloride (CH_2Cl_2) and addition of carbon tetrachloride or petroleum ether afforded white crystals of the product.

In a second reaction, 10 g (15 mmoles) of $(\text{C}_6\text{H}_5)_3\text{SnRe}(\text{CO})_5$ was stirred with excess gaseous, dry HCl in CH_2Cl_2 at room temperature for about one hour. During this period the solution developed a slight yellow coloration. Solvent was then removed at reduced pressure to give a yellowish-white solid which was crystallized from CH_2Cl_2 /petroleum ether to yield 5.5 g (66%) of the product.

Tribromo(pentacarbonylrhenium)tin(IV), $\text{Br}_3\text{SnRe}(\text{CO})_5$:

To a stirred solution of $(\text{C}_6\text{H}_5)_3\text{SnRe}(\text{CO})_5$ (1.5 g , 2.3 mmoles) in CCl_4 (25 ml.) was added approximately 0.5 ml. of bromine at room temperature. The reaction mixture was stirred for 10 minutes during which time a white precipitate formed. The mixture was filtered to give 1.2 g of a pale pink solid which was dissolved in a minimum of CH_2Cl_2 and filtered. Careful addition of n-hexane brought about the slow formation of long white needles (600 mg). Concentration of the mother liquor gave an additional 260 mg. Yield, 860 mg (57%).

Triiodo(pentacarbonylrhenium)tin(IV), $I_3SnRe(CO)_5$:

A CCl_4 solution (50 ml) containing $(C_6H_5)_3SnRe(CO)_5$ (1.35 g, 2 mmoles) and iodine (1.9 g, 9 mmoles) was heated to reflux for 3 hours. The solvent was removed at reduced pressure to yield a red oil. Addition of 25 ml petroleum ether dissolved the oil. The solution was filtered to remove some solid impurity and concentrated to about $\frac{1}{2}$ its original volume. Cooling in the refrigerator ($\sim -20^\circ C$) yielded 670 mg (54%) of yellow crystals. Two recrystallizations from hexane yielded a pure sample of the product.

Triiodo(pentacarbonylmanganese)tin(IV), $I_3SnMn(CO)_5$: Was prepared by refluxing a CCl_4 solution (30 ml.) containing $(C_6H_5)_3SnMn(CO)_5$ (0.55 g, 1 mmole) and I_2 (1.3 g, 10 mmoles) for 6 hours. The red oil obtained after removal of solvent in vacuo was dissolved in petroleum ether, filtered, concentrated and cooled to -20° to give long, bright-yellow needles (480 mg, 69%).

Diphenylchloro(pentacarbonylmanganese)tin(IV), $(C_6H_5)_2(C_6H_5)_2ClSnMn(CO)_5$: A filtered (through glass-wool) THF solution of $NaMn(CO)_5$ (~ 20 mmoles) was slowly added to a THF solution of diphenyltin dichloride (6.88 g, 20 mmoles) at -5° . The reaction mixture was stirred for 20 hr at room temperature. Removal of solvent at reduced

pressure left a green oil, which was taken up in hexane and filtered to remove NaCl. The hexane filtrate was cooled affording white needles 4.6 g (46%). In subsequent preparations yields were increased to 60-70%.

Dimethylchloro(pentacarbonylmanganese)tin(IV),

$(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$: was prepared in a manner similar to that of the phenyl analog. A filtered THF solution (80 ml) containing ~40 mmoles of $\text{NaMn}(\text{CO})_5$ was added slowly to a THF solution (60 ml) of $(\text{CH}_3)_2\text{SnCl}_2$ (8.8 g, 40 mmoles) at 0°. The mixture was allowed to come to room temperature and stirred overnight. After removal of solvent at reduced pressure, an oily residue was obtained. Addition of about 100 ml. of hexane brought about deposition of NaCl which was filtered off. The yellow filtrate was concentrated to a volume of ~50 ml. Cooling of the solution gave long, white needles (11.4 g, 75%) of the product.

Diphenylchloro(pentacarbonylrhenium(tin(IV), $(\text{C}_6\text{H}_5)_2\text{ClSnRe}(\text{CO})_5$:

A solid mixture containing 0.68 g, (1 mmole) of $(\text{C}_6\text{H}_5)_3\text{SnRe}(\text{CO})_5$ and 0.28 g (0.5 mmole) of $\text{Cl}_3\text{SnRe}(\text{CO})_5$ was heated at 150°-160° for 0.5 hr. in an oil bath. Upon cooling, the yellow melt solidified. The solid was extracted with portions of hot hexane totalling about 25 ml. The extracts were filtered on fluted paper and

cooled. Obtained were 630 mg of a white crystalline solid which formed as small nodules in the flask. An infrared spectrum of this material indicated a slight impurity due to unreacted $(C_6H_5)_3SnRe(CO)_5$. Recrystallization from hexane afforded 500 mg of the pure product.

Phenyldichloro(pentacarbonylmanganese)tin(IV),

$(C_6H_5)_2Cl_2SnMn(CO)_5$: Using the procedure prescribed by Gorsich (19), anhydrous hydrogen chloride was bubbled through a solution of $(C_6H_5)_3SnMn(CO)_5$ (5 g , 9.3 mmoles) in 200 ml. of carbon tetrachloride (kept at 0°) for about 45 min. The solvent was removed at 10° to give a white solid having a cheesy odor. Extraction with hot hexane, filtration and cooling gave white, wooly crystals. The product was identified by its melting point (see Table).

Phenyldichloro(pentacarbonylrhenium(tin(IV), $(C_6H_5)_2Cl_2$ -

$SnRe(CO)_5$: 10 g (14.8 mmoles) of $(C_6H_5)_3SnRe(CO)_5$ were dissolved in 250 ml. of carbon tetrachloride and the solution cooled to -7° in an ice-salt bath. Anhydrous hydrogen chloride was bubbled through the solution until a white precipitate began forming (ca. 25 min.). Removal of solvent at reduced pressure and 10° yielded a white solid which was extracted with a mixture of hexane and ligroin. Upon cooling the solution, fine white crystals formed. The solid was filtered, washed with petroleum ether

and dried in a stream of nitrogen. Yield of dry solid 4.3 g (49%). Several recrystallizations of the product from CH_2Cl_2 -pet ether failed to yield a pure product as was evidenced by a wide melting point and extra bands in the carbonyl stretching region of the infrared spectrum. To remove the unidentified impurity the material was dissolved in chloroform and chromatographed using a 1 ft silicic acid column developed in the same solvent. The product was eluted with chloroform requiring 1 hour and 15 min to pass through the column. Its purity was indicated by melting point and infrared spectrum.

Diphenyliodo(pentacarbonylmanganese)tin(IV); $(\text{C}_6\text{H}_5)_2\text{-ISnMn}(\text{CO})_5$: To an acetone (20 ml) solution of $(\text{C}_6\text{H}_5)_2\text{-ClSnMn}(\text{CO})_5$ was added an excess amount of sodium iodide. A yellow coloration and the formation of a fine white precipitate were noted immediately. After brief warming on the steam bath, the mixture was filtered (fluted filter-paper) and the solvent removed at reduced pressure to give an oily solid. Extraction with hexane and recrystallization twice from petroleum ether (bp 30-60) yielded 450 mg of white needles.

Phenyldiiodo(pentacarbonylmanganese)tin(IV); $(\text{C}_6\text{H}_5)_2\text{-I}_2\text{-SnMn}(\text{CO})_5$: A carbon tetrachloride (about 15 ml) solution of $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ (0.94 g, 1.73 mmol) and iodine

(0.88 g , 3.5 mmoles) was stirred magnetically in a glass-stoppered flask for 2 hours at room temperature during which time the purple color had almost disappeared.

Solvent was removed at reduced pressure to give a yellow liquid. The liquid was dissolved in petroleum ether (bp 30°-60°) and cooled to give long, silky needles. Cooling of the mother liquor to -20° gave a further amount of the product. The combined amounts were recrystallized from petroleum ether.

Prepared in an analogous manner was phenyldiiodo (pentacarbonylrhenium(tin(IV)), (C₆H₅)₂I₂SnRe(CO)₅ which was obtained in 49% yield as white needles which were recrystallized from hexane.

Reaction of (C₆H₅)₂SnCl₂ with NaRe(CO)₅: In a reaction analogous to that used for preparation of (C₆H₅)₂ClSnMn(CO)₅, a THF solution containing 20 mmoles of NaRe(CO)₅ was added dropwise to a solution of (C₆H₅)₂SnCl₂ (6.88 g , 20 mmoles) in the same solvent at 0°. The mixture was allowed to come to room temperature and stirred for 23 hours. Solvent was removed in vacuo to give an oil which was dissolved in methylene chloride and filtered to remove NaCl. The oil was obtained again upon removal of solvent but trituration with hexane resulted in crystallization. Extraction of the solid with hexane gave 2.3 g of white crystals which proved to be

$(C_6H_5)_2Sn[Re(CO)_5]_2$ (see Chapter III).

Reaction of $(CH_3)_2SnCl_2$ with $NaRe(CO)_5$: ~ 10 mmoles of $NaRe(CO)_5$ were prepared in 75 ml of THF and added to a THF solution (25 ml) of $(CH_3)_2SnCl_2$ (2.20 g , 10 mmoles) at 0°. Addition was carried out dropwise over a one-hour period after which time the mixture was allowed to come to room temperature and was stirred for approximately eighteen hours. Aliquots of the reaction mixture were taken at one hour and four hours after addition in order to follow the reaction by changes in the infrared spectrum. No changes over the entire reaction time were found. Preliminary infrared and proton nmr spectra of the residue obtained after removal of solvent indicated a highly complex mixture of products. The residue was extracted with warm petroleum ether which provided a yellow solution and a white solid residue. This residue was then extracted with methylene chloride and filtered to give NaCl only as insoluble remainder. Removal of CH_2Cl_2 gave a white solid which was found by infrared to contain no carbonyl-bearing compounds. Nmr showed two resonances at 9.82 τ and 8.77 τ . No further attempt to identify these components was made although it is assumed they were methyltin species.

The petroleum ether extract was taken to dryness to give a yellow solid. The solid was subjected to high

vacuum (0.1 mm) in a sublimator overnight at 50°. This provided a white crystalline sublimate which showed peaks at 2070, 2014, and 1975 cm^{-1} . This corresponded to $\text{Re}_2(\text{CO})_{10}$. An nmr of the solid remaining after sublimation showed five principle components having the following τ values in CDCl_3 : 9.6, 9.35, 9.16, 9.14, 8.67. The values at 9.6 and 9.14 τ correspond to those obtained in the present work for $(\text{CH}_3)_3\text{SnRe}(\text{CO})_5$ and $(\text{CH}_3)_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ respectively. The peak at 9.35 τ corresponded to $(\text{CH}_3)_3\text{SnCl}$ (lit: (72) 9.37). The remaining peaks were not identified.

Reaction of NaI with $\text{Cl}_3\text{SnMn}(\text{CO})_5$: To an acetone (25 ml.) solution of $\text{Cl}_3\text{SnMn}(\text{CO})_5$ (0.84 g , 2 mmoles) was added NaI (1.3 g , 45% xs). The solution became dark-red immediately and a fine, white suspension was produced. The mixture was warmed on a steam bath and filtered. Solvent was removed at reduced pressure to yield a dark-red, oily residue containing some crystalline solid. Extraction with hexane and subsequent removal of solvent gave an orange solid which appeared to be a mixture. Treatment at 0.05 mm and room temperature in a sublimator produced red crystals (110 mg) of what proved to be $\text{ISnMn}(\text{CO})_5$. This was shown by melting point: found, 110-115 dec; lit, (54) 110 dec; and by comparison of infrared stretching frequencies in the terminal carbonyl

region: found, 2125, 2044, 2015 and 2004 cm^{-1} ; lit., (73) 2125.0, 2043.3, 2014.9 and 2003.2 cm^{-1} . The orange residue (460 mg) in the sublimer was recrystallized from petroleum ether to give yellow needles of $\text{I}_3\text{SnMn}(\text{CO})_5$.

TABLE II

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	Mp. °C. ^a	Color	Analyses, %									
			Found					Calculated				
			C	H	O	X ^b		C	H	O	X	
Me ₃ SnMn(CO) ₅ ^c	26-27 ^d	White	27.4	2.9	-----	-----		26.8	2.5	-----	-----	
Me ₂ ClSnMn(CO) ₅	94.5-96.5	White	22.3	1.6	-----	-----		22.2	1.6	-----	-----	
Ph ₂ ClSnMn(CO) ₅	102-103.5	White	41.8	2.0	-----	6.9		40.6	2.0	-----	7.0	1
Ph ₂ ISnMn(CO) ₅	121-123	White	34.6	1.8	13.3	23.3		34.3	1.7	13.5	21.3	50
PhI ₂ SnMn(CO) ₅	90-92	Pale Yellow	22.0	0.8	12.2	38.6		20.5	0.8	12.4	39.4	1
I ₃ SnMn(CO) ₅	78-81	Bright Yellow	8.8	0.1	11.7	55.0		8.7	0.0	11.5	54.8	
Me ₃ SnRe(CO) ₅	51-58	White	19.8	2.0	-----	-----		19.6	1.9	-----	-----	
Ph ₃ SnRe(CO) ₅ ^e	144.5-146	White	41.8	2.8	-----	-----		40.8	2.2	-----	-----	
Ph ₂ ClRe(CO) ₅	116-118	White	32.2	1.6	-----	6.8		32.2	1.6	-----	5.6	
PhCl ₂ Re(CO) ₅	117-119	White	22.4	1.1	13.6	12.2		22.3	0.9	13.5	12.0	
PhI ₂ Re(CO) ₅	119-122	White	17.2	0.8	10.5	32.6		17.0	0.7	10.3	32.7	
Cl ₃ SnRe(CO) ₅	>250 dec ^f	White	11.4	0.0	-----	-----		10.9	0.0	-----	-----	

TABLE II (continued)

Compound	Mp. °C. ^a	Color	Analyses, %							
			Found				Calculated			
			C	H	O	X ^b	C	H	O	X
Br ₃ SnRe(CO) ₅	265 dec ^g	White	9.4	0.1	----	----	8.8	0.0	----	----
I ₃ SnRe(CO) ₅	116-118	Yellow	7.3	0.1	10.0	48.0	7.3	0.0	10.0	46.1
Ph ₃ GeRe(CO) ₅	157.5-158.5 ^h	White	44.0	2.4	----	----	43.8	2.4	----	----
Ph ₃ PbRe(CO) ₅	133-135	Pale Yellow	36.8	2.1	----	----	36.1	2.0	----	----

a. Kofler hot stage.

b. Halogen.

c. Throughout tables in this thesis the groups CH₃ and C₆H₅ will be represented by Me and Ph respectively.

d. Ref. 63.

e. Ref.22: Mp. 142-143.

f. Ref.22: Mp. 220 dec.

g. Ref.22: Mp. 220 dec.

h. Ref.21: Mp. 155.

CHAPTER III

BIS- AND TRIS-(PENTACARBONYLMANGANESE AND -RHENIUM)

DERIVATIVES

Earlier descriptions of tin-manganese and tin-rhenium compounds possessing more than one metal-metal bond are few and have dealt only with their preparation and physical properties.

Compounds of the type $R_2M[Mn(CO)_5]_2$ ($M = Sn, Pb$) were prepared by Gorsich (19). Preparations of $(C_6H_5)_2Sn[Mn(CO)_5]_2$, $Cl_2Sn[Mn(CO)_5]_2$ and $(C_2H_5)_2Pb[Mn(CO)_5]_2$ were described. Analogous derivatives of the type $R_2Sn[Re(CO)_5]_2$ were reported briefly by Nesmeyanov et al. (22).

Systems containing R_2SnMnM groupings are also known. Almost simultaneous reports by Patil and Graham (74) and by Nesmeyanov and coworkers (75) gave preparation, of compounds such as $(CH_3)_2Sn[Mn(CO)_5][Mo(CO)_3(\pi-C_5H_5)]$, $(C_6H_5)_2Sn[Mn(CO)_5][Re(CO)_5]$ and $(C_6H_5)ClSnCo(CO)_4[Mn(CO)_5]$.

All preparations of the "bis" compounds involved reaction of the metal carbonyl anion with the organotin halide and, in the case of the halo-derivatives, subsequent cleavage of the phenyl groups with hydrogen chloride or bromine.

The only two previously mentioned tris(metal carbonyl) tin compounds are due to Nesmeyanov (22). One,

$\text{C}_6\text{H}_5\text{Sn}[\text{Re}(\text{CO})_5]_3$, was obtained by replacement of bromine in $(\text{C}_6\text{H}_5)_2\text{Br}_2\text{SnRe}(\text{CO})_5$ by $\text{Re}(\text{CO})_5$ groups. The other, the bromo derivative, was prepared either by reaction of $\text{NaRe}(\text{CO})_5$ with $\text{Br}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ or by cleavage of the phenyl group in $\text{C}_6\text{H}_5\text{Sn}[\text{Re}(\text{CO})_5]_3$. Spectroscopic data on the bis- and tris- derivatives was almost non-existent and required reinvestigation and expansion.

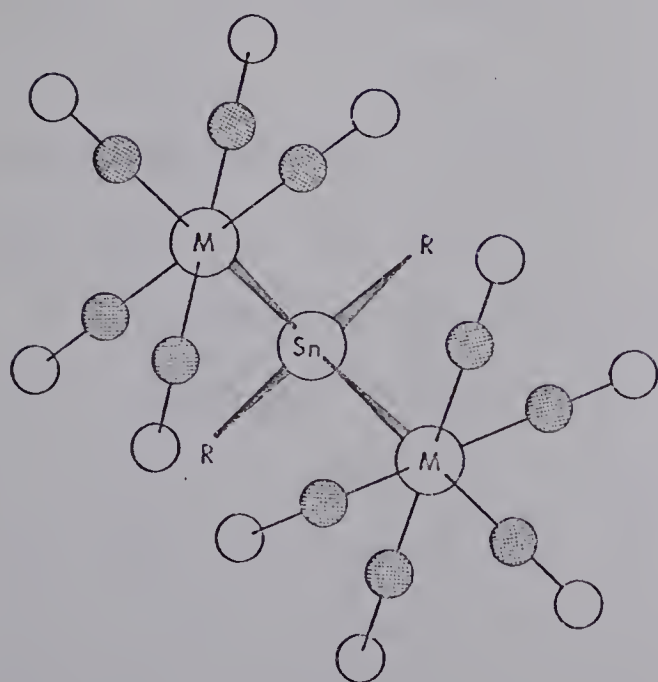
Structures of Bis- and Tris- derivatives

Structural information on these compounds centers around three reports. Kilbourn and Powell (76) found that in $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$, both metal-metal bonds were 2.70 \AA long with an angle of approximately 117° between the three metals. A slightly longer Sn-Mn bond of 2.73 \AA was found in the compound $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{Mn}(\text{CO})_5][\text{Co}(\text{CO})_4]$, (77) the Sn-Co distance in the same compound being 2.66 \AA . A Co-Sn-Mn angle of 114° was found.

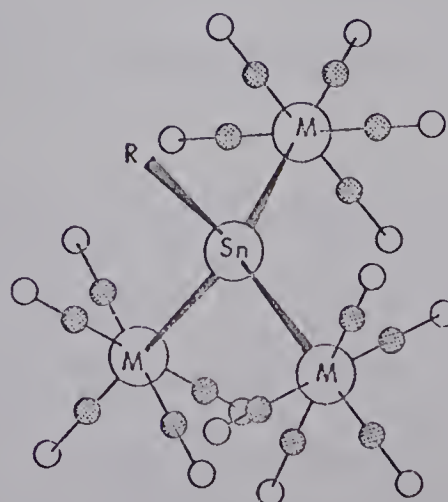
Recently, Tsai and coworkers (78) reported the crystal structure of $\text{ClSn}[\text{Mn}(\text{CO})_5]_3$ which they had prepared independently. A mean metal-metal distance of 2.737 \AA was determined for this material. This finding was in accord with a trend to longer bond lengths with each successive $\text{Mn}(\text{CO})_5$ substituent on tin and possibly represents the effect of the presence of a third bulky group.

<u>Compound</u>	<u>Metal-Metal Bond</u>	<u>Ref.</u>
	<u>Length in Å</u>	
$(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$	2.63 ± 0.01	50
$(C_6H_5)_3SnMn(CO)_5$	2.674 ± 0.004	67
$(CH_3)_3SnMn(CO)_5$	2.674 ± 0.004	68
$(C_6H_5)_2Sn[Mn(CO)_5]_2$	2.70 ± 0.01	76
$ClSn[Mn(CO)_5]_3$	2.737 ± 0.01	78
$(C_6H_5)_2Sn[Mn(CO)_5][Co(CO)_4]$	2.73 ± 0.01	77

As expected, the tin atoms retained basic tetrahedral coordination while the groups around manganese were octahedrally disposed. Representative structures of the bis- and tris compounds are shown in VII and VIII.



VII

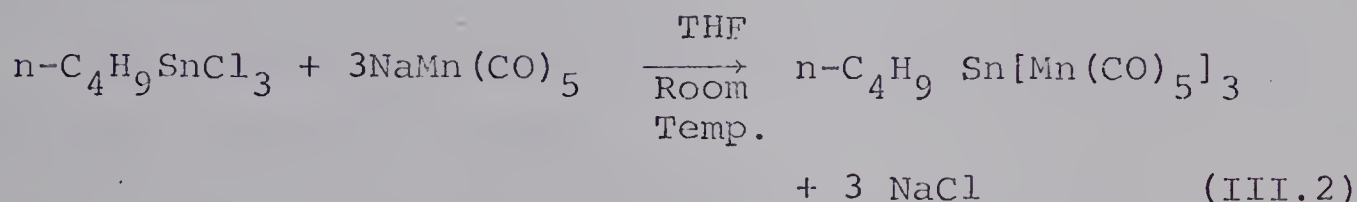
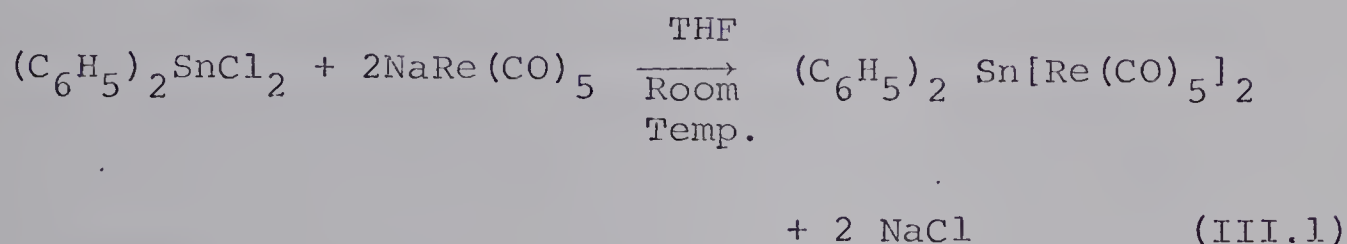


VIII

M = Mn, Re
 ○ OXYGEN
 ● CARBON

RESULTS AND DISCUSSION

In preparing the bis- and tris-(metal carbonyl) tin species, the same techniques as used in Chapter II were employed. Reaction of either $\text{NaRe}(\text{CO})_5$ or $\text{NaMn}(\text{CO})_5$ with R_2SnCl_2 or RSnCl_3 in THF under a nitrogen atmosphere produced the desired compounds containing 3 and 4 metal atoms:

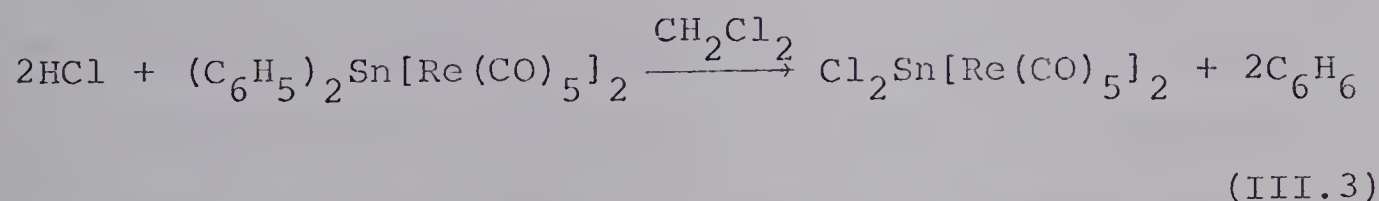


The reactions were straight-forward and were usually complete within 30 minutes to an hour after mixing of the two reagents. As was the case with the mono-derivatives, an immediate color change of the anion solutions indicated the speed of the reaction.

Nesmeyanov (22) obtained $\text{C}_6\text{H}_5\text{Sn}[\text{Re}(\text{CO})_5]_3$ by treating the $(\text{C}_6\text{H}_5)_2\text{Br}_2\text{Sn-}$ compound with 2 moles of the anion. In this present work use of $\text{C}_6\text{H}_5\text{SnCl}_3$ as starting material was much more convenient; the convenience being due in part to the presence of a large supply of the trihalide.

The only starting material that presented some difficulty was CH_3SnCl_3 . Commercial samples supplied by Alfa Inorganics were highly impure. Large amounts of $(\text{CH}_3)_2\text{SnCl}_2$ were found in supposed pure material. The pure compound was finally prepared using Smith and Rochow's (79) procedure of bubbling gaseous methyl chloride through molten (365°) stannous chloride. This proved to be an arduous process. The product which sublimed from the hot reaction vessel was collected on a water-cooled cold-finger. One day of continuous operation produced about four grams of product.

The dichlorotin derivatives were obtained easily by hydrogen chloride cleavage:



As in the case of $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ reaction time was short. Chlorine was not investigated as a possible cleavage reagent since Gorsich (19) had shown earlier that Sn-Mn bond fission occurred to a marked degree. This fact is indicative of the increased reactivity possessed by systems having more than one tin-manganese bond.

Compounds of the series $\text{XSn}[\text{M}(\text{CO})_5]_3$ (where $\text{X} = \text{Cl}, \text{Br}$) were best prepared by reaction of excess anion with

the respective tin tetrahalide. Stannic chloride and bromide are fairly reactive species which hydrolyze easily in moist air. They were used in the present work in both the free form and also as the THF adduct, $\text{SnX}_4 \cdot 2\text{THF}$, which is a white solid soluble in excess of the solvent. The intense red color obtained in reaction mixtures of SnCl_4 or SnBr_4 with $\text{NaM}(\text{CO})_5$ is partly due to the products XSnM_3 . However, a dark red oil was obtained also after separation of these products. Attempts of obtaining crystalline material failed. In one reaction, an attempt to obtain the SnM_4 series was made. Refluxing SnBr_4 with an excess of $\text{NaMn}(\text{CO})_5$ gave $\text{BrSn}[\text{Mn}(\text{CO})_5]_3$ plus a large amount of the red oil which was thought at the time to possibly contain the tetrakis-species. However infrared spectra showed only $\text{Mn}_2(\text{CO})_{10}$ and attempts at recrystallization gave only $\text{Mn}_2(\text{CO})_{10}$ and insoluble decomposition materials. Only two SnM_4 species are known. One is $\text{Sn}[\text{Fe}(\text{CO})_4]_4$ (26) (prepared by Stone et al.) which also possesses Fe-Fe bonds and the other is $\text{Sn}[\text{Co}(\text{CO})_4]_4$ prepared by D. J. Patmore (80). An SnMoFe_2 (17) system is also known; however because the metals are not all the same it will not be considered in the same class of compounds. Tsai (78) mentioned "two other unidentifiable components" in his preparation of $\text{ClSn}[\text{Mn}(\text{CO})_5]_3$. Possibly one of these was the elusive SnMn_4 system. The fact that it would not be made (by this method) may indicate the

high degree of steric hindrance that would exist with four $\text{Mn}(\text{CO})_5$ groups packed around tin. $\text{Co}(\text{CO})_4$ groups are smaller and might fit more easily.

Generally, the bis-metal carbonyl derivatives are stable to light and air in the solid form; however, they do oxidize slowly in solution. The rhenium derivatives are somewhat more stable, having higher melting points.

Solubilities follow the same trend as in $\text{R}_3\text{SnM}(\text{CO})_5$ species. The phenyl and methyl compounds can be crystallized easily from hexane. However dichloro species are insoluble in this solvent and will dissolve only in more polar media such as methylene chloride and alcohol.

The tris-derivatives as a class exhibit somewhat different properties. They are all, without exception, highly colored, colors ranging from bright yellow to red. Nesmeyanov (22) reported that $\text{BrSn}[\text{Re}(\text{CO})_5]_3$ was white. Although this particular compound was not prepared in the present work, there is no apparent reason why it should differ from ClSnRe_3 , ClSnMn_3 , BrSnMn_3 and ISnMn_3 which are all orange or red and indeed shift towards the red from chloride to iodide. There is perhaps some justification for suspecting that the compound reported (22) was not $\text{BrSn}[\text{Re}(\text{CO})_5]_3$.

All members of the series are extremely beautiful crystalline compounds. They are markedly less stable in the solid form. Samples stored in the dark over

periods of months show a tendency to become darker in color. In solution, decomposition is pronounced and accounts for lowered yields on recrystallization. Over a period of minutes solutions in light become cloudy and lose color. This tendency is most apparent if hydrocarbon solvents (in which solubility is only moderate at best) are used. Surprisingly, the ClSnRe_3 compound could be recrystallized from acetone-water mixtures without noticeable hydrolysis over short periods of time. This resistance to hydrolysis which bis- and mono- derivatives undergo readily may be due to the halide being 'buried' by the bulky metal carbonyl groups around the central tin atom.

The infrared and proton nmr spectra of these compounds are discussed in Chapters VII and VIII.

EXPERIMENTAL SECTION

Analyses, molecular weights, melting points and exact masses were obtained as given in Chapter II.

Solvents were used as described previously. $(\text{CH}_3)_2\text{SnCl}_2$, $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$, $\text{C}_6\text{H}_5\text{SnCl}_3$ and $n\text{-C}_4\text{H}_9\text{SnCl}_3$ were obtained commercially from M and T Chemicals, Inc., Rahway, N. J. CH_3SnCl_3 (78), $\text{CH}_2 = \text{CHSnCl}_3$ (81) and SnBr_4 (82) were prepared using published procedures.

Fisher Certified Reagent SnCl_4 was used as obtained.

Analyses and physical properties are given in Table IV.

Diphenylbis(pentacarbonylrhenium)tin(IV), $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{Re}(\text{CO})_5]_2$: Rhenium carbonyl (7.5 g , 11.5 mmoles) in 100 ml of THF was stirred over 20 ml of 1% sodium amalgam for 1 hr. After removal of the amalgam, $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ (3.0 g , 11.0 mmoles) was added and the mixture was stirred at room temperature for 20 min. The solution was concentrated to about 60 ml on a rotary evaporator and then poured into ice-water. The white, crystalline precipitate was filtered, washed twice with water, and dried under vacuum. Recrystallization from n-hexane afforded white plates (5.3 g , 52%).

Prepared in a similar manner was Dimethylbis-(pentacarbonylrhenium)tin(IV), $(\text{CH}_3)_2\text{Sn}[\text{Re}(\text{CO})_5]_2$; although in this case the THF was entirely removed at reduced pressure and the product extracted with n-hexane.

Dichlorobis(pentacarbonylrhenium)tin(IV), $\text{Cl}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$:

Anhydrous HCl was bubbled through a solution of $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ (2.0 g , 2.2 mmoles) in dichloromethane (40 ml) at room temperature for 15 minutes, during which the solution became yellow. After stirring for an additional 30 minutes, solvent was removed at reduced pressure

TABLE III

REACTION CONDITIONS FOR PREPARATION OF $\text{Rsn}[\text{M}(\text{CO})_5]_3$

Compound	Mmoles Used		Reaction Time (min)	Crystallization Solvent(s)	Remarks
	$\text{NaM}(\text{CO})_5$	RsnCl_3			
$\text{PhSn}[\text{Mn}(\text{CO})_5]_3$	15.3	4.6	60	Ligroin	Solvent decanted and crystals washed in pentane.
$\text{ViSn}[\text{Mn}(\text{CO})_5]_3$	15.3	4.6	30	Ligroin	Sp. Gr. of ViSnCl_3 : 2.0.
$\text{MeSn}[\text{Mn}(\text{CO})_5]_3$	15.3	5.0	20	1. Hot hexane 2. Acetone- H_2O	
$\text{n-BuSn}[\text{Mn}(\text{CO})_5]_3$	13.8	4.6	60	Hot hexane	See experimental section for full description.
$\text{PhSn}[\text{Re}(\text{CO})_5]_3$	9.2	3.0	30	Acetone- H_2O	Reaction mixture poured on to ice-water.
$\text{n-BuSn}[\text{Re}(\text{CO})_5]_3$	9.2	2.9	30	1. Acetone- H_2O 2. Hot ligroin	
$\text{ViSn}[\text{Re}(\text{CO})_5]_3$	9.2	2.9 (0.36ml)	30	Benzene-ligroin	Crystals obtained by concentrating solution in N_2 stream

(rotary evaporator). Recrystallization of the residue from dichloromethane-petroleum ether (30-60) afforded 1.02 g (55%) of white needles.

Preparation of $\text{RSn}[\text{M}(\text{CO})_5]_3$ ($\text{R}=\text{CH}_3, n\text{-C}_4\text{H}_9, \text{CH}_2=\text{CH}, \text{C}_6\text{H}_5$; $\text{M}=\text{Mn}, \text{Re}$): Since the same basic procedure was used in preparing the eight compounds of this class, the detailed description of one preparation is given below. The remaining members of the series are reported in Table III which gives reaction time, amounts used and recrystallization solvent.

$n\text{-Butyltris}(\text{pentacarbonylmanganese})\text{tin(IV)}, n\text{-C}_4\text{H}_9\text{Sn}[\text{Mn}(\text{CO})_5]_3$:

To 13.8 mmoles (3 g) of $\text{NaMn}(\text{CO})_5$ in 50 ml of THF was added 1.29 g (4.6 mmoles) of $n\text{-C}_4\text{H}_9\text{SnCl}_3$ (weighed as the liquid) in 5 ml of THF. The reaction mixture became lighter in color. The mixture was stirred magnetically for one hour at room temperature. THF was removed at reduced pressure to give an orange-yellow solid residue. The solid was washed with a pentane (~ 5 ml) and filtered to give 1.95 g (56%) of a yellow solid. Recrystallization from hot hexane gave 1.05 g of bright yellow crystals.

$\text{Chlorotris}(\text{pentacarbonylmanganese})\text{tin(IV)}, \text{ClSn}[\text{Mn}(\text{CO})_5]_3$:

A. Using a Stoichiometric Amount of $\text{NaMn}(\text{CO})_4$

A white slurry of the THF adduct, $\text{SnCl}_4 \cdot 2\text{THF}$, was prepared by addition of 0.6 ml (1.34 g, 5.1 mmoles) of

SnCl_4 (Sp gr 2.23) to 25 ml of THF at 0° . To the slurry was added from an addition funnel a THF solution of $\text{NaMn}(\text{CO})_5$ (3.35 g , 15.3 mmoles). A yellow color gradually developed. The 0° bath was removed and the reaction mixture allowed to come to room temperature (28°). After about 20 minutes it had become more orange in appearance. The mixture was filtered on Büchner funnel and the NaCl obtained washed with THF. The filtrate was stripped of solvent to give an oil which solidified quickly. The orange solid was extracted with a hot mixture of ligroin and benzene. On cooling a mixture of yellow and orange crystals were obtained. Recrystallization from benzene-hexane gave yellow needles and orange prisms. Using an alumina column (Shawinigan acid washed) developed in hexane, the orange fraction was eluted in benzene and the yellow in THF. The latter compound was identified as $\text{Cl}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ from its published melting point (19) (found 144.5-146; lit. 143-144) and by a comparison of its infrared spectrum with that of $\text{Cl}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$.

B. Using an Excess of $\text{NaMn}(\text{CO})_5$

The above reaction was repeated using 0.4 ml (3.4 mmoles) of SnCl_4 added directly to a solution (30 ml) of $\text{NaMn}(\text{CO})_5$. The mixture became dark red. After stirring for one hour, the mixture was filtered and solvent was removed to give a red oil. Addition of pentane to the oil induced formation

an orange solid. The pentane was decanted and the solid dissolved in a hot benzene-ligroin mixture. Concentration and cooling of the orange solution gave 1.12 g of orange needles.

Chlorotris(pentacarbonylrhenium)tin(IV), $\text{ClSn}[\text{Re}(\text{CO})_5]_3$:

To a THF (30 ml) solution of $\text{NaRe}(\text{CO})_5$ was added a slurry of $\text{SnCl}_4 \cdot 2\text{THF}$ contained in 15 ml of the same solvent. The reaction mixture immediately became dark red. It was stirred for 2 hours at room temperature then stored overnight in the refrigerator. Filtration to remove NaCl and subsequent removal of solvent produced a red oil which precipitated more NaCl. A second filtration and removal of solvent gave an orange solid which was recrystallized by dissolving in a small amount of warm acetone and slow drop-by-drop addition of water to give yellow crystals.

Iodotris(pentacarbonylmanganese)tin(IV), $\text{ISn}[\text{Mn}(\text{CO})_5]_3$:

Addition of NaI (0.2 g , 1.3 mmole) to a THF (10 ml) solution of $\text{ClSn}[\text{Mn}(\text{CO})_5]_3$ (0.7 g , 1 mmole) resulted in a darkening of the solution from yellow to amber. Removal of the solvent gave a red solid. The solid was dissolved in methylene chloride and centrifuged to separate a fine suspension of NaCl. Hexane was added and the solution cooled to give large red crystals of the product.

Reaction of Stannic Bromide with $\text{NaMn}(\text{CO})_5$: To a THF solution (80 ml) of $\text{NaMn}(\text{CO})_5$ prepared from 7.8 g (20 mmoles) of $\text{Mn}_2(\text{CO})_{10}$ was added gradually to a THF solution (60 ml) of SnBr_4 (3.9 g , 8.9 mmoles). The color became darker as addition progressed. The mixture was stirred (magnetically) overnight at room temperature then refluxed for one hour. Solvent was removed from the dark red mixture to give an oil which was extracted with hot hexane. The yellow hexane extract provided 0.8 g of an orange solid which was shown by infrared to consist mainly of $\text{Mn}_2(\text{CO})_{10}$. The remaining oil was dissolved in CH_2Cl_2 . Addition of petroleum ether (30-60) again gave an oil. The oil was triturated with methanol which caused an orange precipitate to form while the dark red color remained in solution. Recrystallization of the orange solid from acetone-water provided fine orange crystals of $\text{BrSn}[\text{Mn}(\text{CO})_5]_3$. The remaining red material was placed under high vacuum for about fifteen minutes after solvent removal. The bronze colored material obtained showed only $\text{Mn}_2(\text{CO})_{10}$ in the infrared. Attempts at recrystallization resulted in more carbonyl and no other identifiable products.

TABLE IV

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	Mp. °C.	Color	Analyses, %					
			Found			Calculated		
			C	H	O	C	H	O
$\text{Ph}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ ^a	135-138	White	28.3	1.3	----	28.5	1.1	----
$\text{Me}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ ^b	119-121	Pale Yellow	19.3	1.0	19.8	18.0	0.8	20.0
$\text{Cl}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ ^c	171-172	White	14.9	0.3	----	14.3	0	----
$\text{PhSn}[\text{Mn}(\text{CO})_5]_3$ ^d	130-140 dec	Orange-Yellow	32.2	0.9	28.3	32.3	0.6	30.7
$\text{n-BuSn}[\text{Mn}(\text{CO})_5]_3$ ^e	143-145	Yellow	29.9	1.2	29.0	30.0	1.2	31.6
$\text{MeSn}[\text{Mn}(\text{CO})_5]_3$	120-155 dec	Yellow	28.3	0.3	30.5	26.7	0.4	33.4
$\text{ViSn}[\text{Mn}(\text{CO})_5]_3$ ^f	120-140 dec	Yellow	28.6	0.4	30.0	28.0	0.4	32.9
$\text{ClSn}[\text{Mn}(\text{CO})_5]_3$ ^g	175-176 dec	Orange	24.8	0.0	31.1	24.4	0.0	32.5
$\text{BrSn}[\text{Mn}(\text{CO})_5]_3$ ^h	185-187 dec	Orange	23.0	0.0	30.5	23.0	0.0	30.6
$\text{ISn}[\text{Mn}(\text{CO})_5]_3$ ⁱ	178 dec	Red	22.9	0.0	28.3	21.7	0.0	28.9
$\text{PhSn}[\text{Re}(\text{CO})_5]_3$ ^j	> 195 dec	Yellow	22.1	0.5	20.5	21.5	0.4	20.4
$\text{n-BuSn}[\text{Re}(\text{CO})_5]_3$	165-166	Yellow	20.4	0.9	21.2	19.8	0.8	20.8

TABLE IV (continued)

Compound	Mp. °C.	Color	Analyses, %					
			Found			Calculated		
			C	H	O	C	H	O
ViSn[Re(CO) ₅] ₃	175-200 dec	Yellow	18.6	0.2	21.2	18.3	0.3	21.5
MeSn[Re(CO) ₅] ₃	160-165 dec	Yellow	17.7	0.1	21.4	17.3	0.3	21.6
ClSn[Re(CO) ₅] ₃ ^k	193-196 dec	Yellow	16.9	0.4	21.0	15.9	0.0	21.2

- a. Lit. 139°: Ref. (22)
- b. Mol. wt.: calculated 490; found, 449 in dibromomethane.
- c. Mol. wt.: calculated, 842; found, 807 (CH₂Br₂). Cl: calculated, 8.4; found, 8.5, 8.3.
- d. Mol. wt.: calculated, 781; found, 786 (CH₂Br₂).
- e. Mol. wt.: calculated, 761; found, 777.
- f. Vi = CH₂ = CH-. Mol. wt.: calculated, 731; found, 729.

TABLE IV (continued)

- g. Cl: calculated, 4.8; found, 3.9.
- h. Br: calculated, 10.2; found, 10.1.
- i. Exact mass: calculated for $^{127}\text{I}^{120}\text{Sn}^{55}\text{Mn}_3$ fragment, 411.6209;
found, 411.6209.
- j. Lit. mp 189; see footnote a.
- k. Cl: calculated, 3.1; found, 4.1.

CHAPTER IV

PENTAFLUOROPHENYL DERIVATIVES

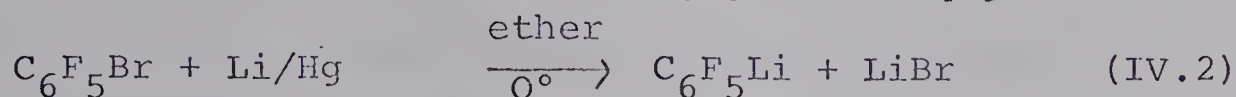
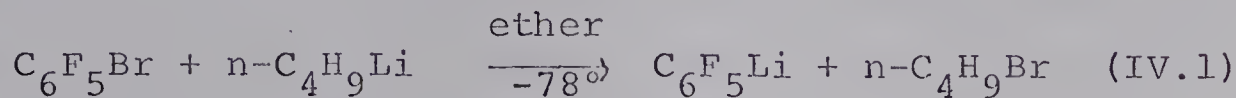
In this chapter the preparation of the first known compounds of pentafluorophenyltin moieties bonded to a metal carbonyl will be discussed.

The first reports of pentafluorophenyltin compounds came in 1963 from two independent investigations. Holmes et al. (83) and Chambers and Chivers (84) both described preparation of compounds of the type $R_n\text{Sn}(\text{C}_6\text{F}_5)_{4-n}$ (R = alkyl, aryl; n = 1-4). Later reports (85,86) from the same two sources described some halo and hydroxy derivatives such as $(\text{C}_6\text{F}_5)_3\text{SnCl}$, $(\text{C}_6\text{F}_5)_2\text{SnCl}_2$ and $(\text{C}_6\text{F}_5)_3\text{SnOH}$. Studies by Tamborski (87) and coworkers have shown that pentafluorophenyl derivatives of tin as well as of germanium and lead are equally or more stable than hydrocarbon analogs.

Many pentafluorophenyl derivatives of both main group and transition metals are known. In most cases one or both of two preparative methods have been used. These methods involve the intermediates $\text{C}_6\text{F}_5\text{MgBr}$ and $\text{C}_6\text{F}_5\text{Li}$. The Grignard reagent was first prepared in 1959 (88,89) and was used to prepare the first metal derivatives. It is obtained by the reaction of magnesium with $\text{C}_6\text{F}_5\text{Br}$ in ethyl ether and has the advantage

of needing only room temperature conditions.

Preparation of C_6F_5Li was first reported in 1962 by Coe, Stephens and Tatlow (90). It was obtained either by a transmetallation reaction (equation IV.1) or by direct metallation using lithium amalgam (IV.2)



Harper et al. (91) prepared the intermediate in good yield using pentafluorobenzene instead of the bromide. At higher temperatures (above 0°) C_6F_5Li becomes unstable and fluorine cleavage occurs. This fact necessitates preparation at low temperatures (-65° to -78°).

To a limited extent, pentafluorophenyl compounds of tin and other metals have been used as sources of the C_6F_5 group. Treichel, Chaudhari and Stone (92) used $(C_6F_5)_2Ti(C_5H_5)_2$ to prepare $C_6F_5BCl_2$:



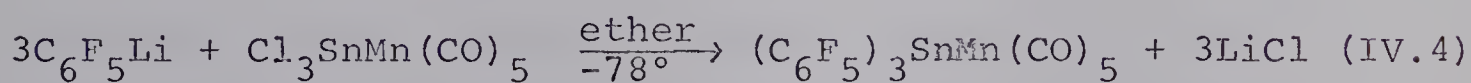
In a similar reaction, $C_6F_5BF_2$ and $(CH_3)_3SnBF_4$ were obtained from the reaction of $(CH_3)_3SnC_6F_5$ with BF_3 (85).

RESULTS AND DISCUSSION

Two preparative routes to preparation of the pentafluorophenyltin compounds obtained in this work were available. The first involved preliminary preparation

of pentafluorophenyltin halides, $(C_6F_5)_n SnCl_{4-n}$ ($n=1-4$), and subsequent reaction of these with the metal carbonyl anion. The alternative route was to react C_6F_5MgBr or C_6F_5Li with the metal carbonyltin halide. It was decided to use the second of these two routes after perusal of the literature (85,86) indicated that the pentafluorophenyltin halides were difficult to prepare in pure and large quantities.

Where C_6F_5Li was used, reactions were necessarily carried out at -78° . The halogentins species was added to the essentially clear ethereal solution of the lithio reagent to produce an initial bright yellow coloration. Upon warming to room temperature a deposit of $LiCl$ formed indicating reaction had occurred. A typical reaction using C_6F_5Li is represented in equation IV.4.

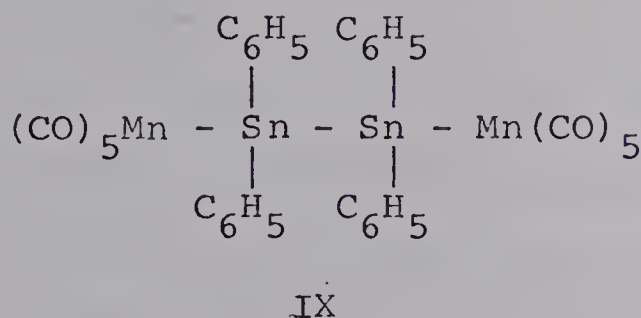


In cases where the Grignard reagent, C_6F_5MgBr , (equation IV.5) was employed, reactions were carried out at room temperature. It was necessary to use a large excess of the Grignard because of by-products that are formed.

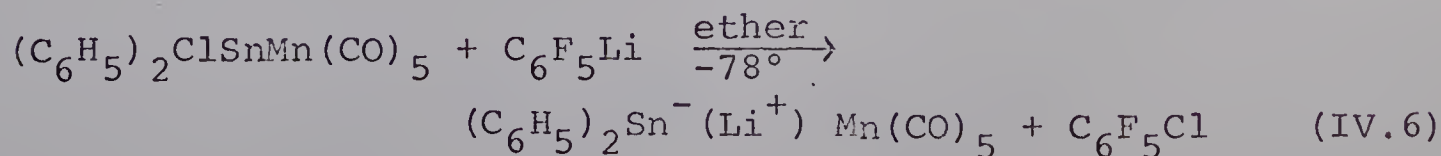


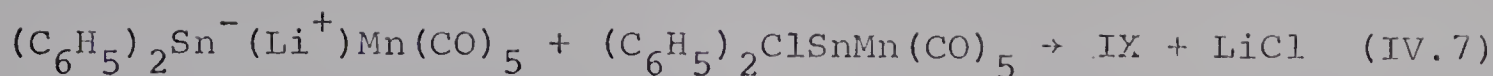
Work-up of the reaction mixtures was complicated by these impurities which appeared as dark materials in the crude product. The impurities were removed by treatment with activated charcoal.

With $\text{C}_6\text{F}_5\text{Li}$, $(\text{C}_6\text{H}_5)_2\text{ClSnMn}(\text{CO})_5$ gave two products in about equal amounts. One was the expected fluoroaryl derivative and the other (easily separated because of lower solubility in hydrocarbon solvents) proved, by complete elemental analysis to be the novel dimeric compound, IX. As can be seen, this compound possesses a



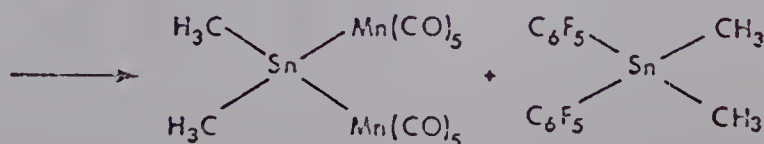
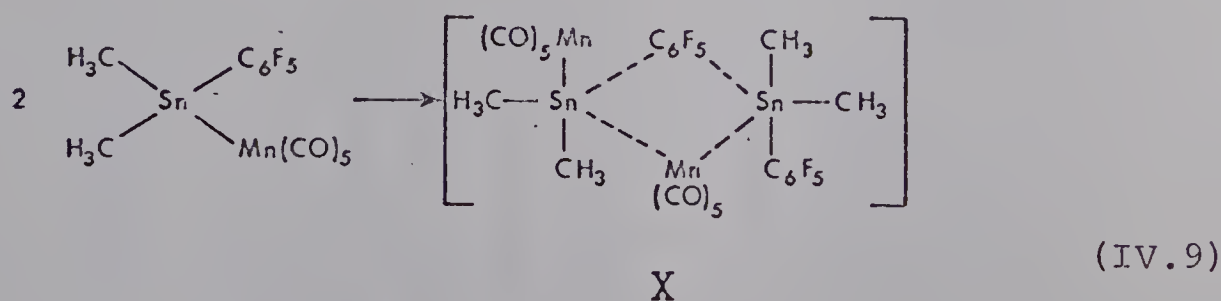
four-metal chain. Only two similar compounds have been reported previously; compounds formulated as $[(\text{CO})_5\text{Re}]_3\text{-Sn-Sn}[\text{Re}(\text{CO})_5]_3$ (22) and $[(\text{C}_6\text{H}_5)_2\text{GeMn}(\text{CO})_5]_2$ (70). The latter compound was obtained by reaction of $(\text{C}_6\text{H}_5)_2\text{GeCl}_2$ with $\text{NaMn}(\text{CO})_5$. A reaction sequence for the formation of II is suggested in equations IV.6 and IV.7.





Reaction IV.6 is analogous to the transmetallation which produced $\text{C}_6\text{F}_5\text{Li}$. It is thought that this reaction occurs initially at -78° to give the bright yellow color that was observed. No LiCl precipitate was noted until temperatures above -25° were reached, indicating that probably it was at this point that the lithio-tin species began reacting with more of the tin halide and with $\text{C}_6\text{F}_5\text{Cl}$. The pentafluorophenyltin product could have been formed in this manner or by in a concurrent displacement of chloride by $\text{C}_6\text{F}_5\text{Li}$.

Reaction of $\text{C}_6\text{F}_5\text{Li}$ or $\text{C}_6\text{F}_5\text{MgBr}$ with $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ failed to result in the desired $\text{C}_6\text{F}_5\text{-Sn}$ derivative. Instead, $(\text{CH}_3)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ and $(\text{CH}_3)_2\text{Sn}(\text{C}_6\text{F}_5)_2$ were obtained as the two major products. It is assumed that the desired compound was formed initially but underwent a disproportionation reaction involving a 5-coordinate tin intermediate (X) (equation IV.9)



The four pentafluorophenyltin derivatives prepared in this work were obtained as white or pale yellow crystalline solids which are stable to light and air over extended periods of time. They are soluble in most organic solvents and in solution will decompose slowly on exposure to light and air. Some difficulty was met in obtaining good crystals, presumably a result of molecular asymmetry caused by the bulky C_6F_5 groups.

The compound IX was somewhat less stable. Even in the solid state, darkening occurred over a few weeks if kept in light.

EXPERIMENTAL SECTION

All analyses, melting points and molecular weights were obtained as described in Chapter II.

Pentafluorophenyl bromide, C_6F_5Br , was obtained commercially from Imperial Smelting Corporation, London, England and used without further purification. n-Butyllithium, $n-C_4H_9Li$, was supplied by the Foote Mineral Co., Exton, Pa.

Published procedures were used in preparing C_6F_5Li (91) and C_6F_5MgBr (89). For the latter material, anhydrous ether and magnesium metal turnings from Mallinckrodt Chemical Works, St. Louis, Mo. were used.

The metal carbonyl starting materials were prepared using procedures given in Chapter II or those given by Gorsich (19).

Analyses and physical properties are shown in Table V.

Infrared stretching frequencies are given in Chapter VII.

Phenylbis(pentacarbonylmanganese)tin (IV), $(C_6F_5)_2C_6H_5-SnMn(CO)_5$:

C_6F_5MgBr was prepared by reaction of C_6F_5Br (3.7 g, 15 mmoles) with magnesium (15 mmoles) in 50 ml of ether. To the deep brown Grignard solution was added (as the solid) $C_6H_5Cl_2Mn(CO)_5$ (4.6 g, 10 mmoles). After stirring for 4.5 hours at room temperature, the mixture was hydrolyzed with about 15 ml of dilute (~ 0.1 molar) hydrochloric acid. The ether layer was dried over Na_2SO_4 for several hours, filtered and the solvent removed on the rotary evaporator to give a dark oil. The oil was dissolved in petroleum ether ($30^\circ-60^\circ$). To remove dark impurities, the solution was treated with activated charcoal, filtered, and concentrated. Upon cooling to -20° , an oil separated which gradually crystallized. Recrystallization from 95% alcohol afforded fine white needles of the product.

Tris(pentafluorophenyl)(pentacarbonylmanganese)tin (IV), $(C_6F_5)_3SnMn(CO)_5$:

A suspension of $Cl_3SnMn(CO)_5$ (2.1 g, 5 mmoles) in 25

ml of ether was added dropwise to a -78° solution of $\text{C}_6\text{F}_5\text{Li}$ (17 mmoles, prepared from $\text{C}_6\text{F}_5\text{Br}$ and a 15.2% solution of $n\text{-C}_4\text{H}_9\text{Li}$ in n -hexane) in 55 ml of ether, and the mixture was stirred for 2.5 hr at -78° , after which an essentially clear yellow solution was observed. A fine white suspension of LiCl formed as the solution warmed to room temperature. After filtration, solvent was removed at reduced pressure leaving a yellow oil, insoluble in petroleum ether. After addition of a small amount of ethyl ether, the solution was again filtered to remove LiCl , concentrated, and cooled to give pale yellow crystals of the product.

Bis(pentafluorophenyl)bis(pentacarbonylmanganese)tin(IV),

$(\text{C}_6\text{F}_5)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$:

Solid $\text{Cl}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ (2.8 g , 5 mmoles) was added directly to a magnetically stirred solution of $\text{C}_6\text{F}_5\text{Li}$ (11 mmoles) in 70 ml of ether at -78° . Stirring was continued at this temperature for two hours. The mixture was brought to room temperature and filtered, and solvent was removed at reduced pressure leaving an oil which was insoluble in petroleum ether. Addition of a few milliliters of ether induced crystallization. Recrystallization from benzene-hexane afforded white prisms of the product (yield 1.3 g).

Reaction of $\text{C}_6\text{F}_5\text{Li}$ with $(\text{C}_6\text{H}_5)_2\text{ClSnMn}(\text{CO})_5$:

A solution of $(\text{C}_6\text{H}_5)_2\text{ClSnMn}(\text{CO})_5$ (5.0 g , 10 mmoles) in 40 ml of ether was added dropwise to a -78° solution of $\text{C}_6\text{F}_5\text{Li}$ prepared from $\text{C}_6\text{F}_5\text{Br}$ (2.72 g , 11 mmoles) in 15 ml of ether and n-butyllithium (11 mmoles, 6.9 ml of hexane solution). The -78° bath was then replaced by one at 0° . As the mixture warmed, it became bright yellow and a fine white precipitate appeared. Magnetic stirring was continued for 30 minutes at 0° and one additional hour at room temperature. The white solid was filtered off and the yellow filtrate was evaporated at reduced pressure to give an oil; addition of petroleum ether gave white crystals of $[(\text{C}_6\text{H}_5)_2\text{SnMn}(\text{CO})_5]_2$, which were recrystallized from hexane. The petroleum ether solution was concentrated and cooled to -78° affording white crystalline $(\text{C}_6\text{H}_5)_2(\text{C}_6\text{F}_5)\text{SnMn}(\text{CO})_5$, which was recrystallized from petroleum ether.

Reaction of $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ with $\text{C}_6\text{F}_5\text{Li}$:

A solution of $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ (3.8 g , 10 mmoles) in 60 ml of ether was added slowly at -78° to a stirred solution of $\text{C}_6\text{F}_5\text{Li}$ (11 mmoles) in 20 ml of ether. An intense yellow coloration developed and a white precipitate appeared. The mixture was stirred one hour, and filtered, and solvent removed affording an oil. Slow addition of petroleum ether gave white crystals, recrystallized from petroleum ether, m.p $104-105^\circ$; the melting point (19) and infrared spectrum (see Chapter VII) of this material showed that

it was $(\text{CH}_3)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$. Solvent was removed from the mother liquor leaving an oil which consisted mainly of $(\text{CH}_3)_2\text{Sn}(\text{C}_6\text{F}_5)_2$, as shown by the nmr spectrum (main peak at τ 9.1 and characteristic methyltin satellites with $J(^{119}\text{Sn}-\text{CH}_3) = 65$ cps (93)).

Reaction of $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ with $\text{C}_6\text{F}_5\text{MgBr}$:

Solid $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ (2.5 g., 6.6 mmoles) was added to 7 mmoles of $\text{C}_6\text{F}_5\text{MgBr}$ in 50 ml of ether. After stirring four hours at room temperature the mixture was hydrolyzed with water, and the ether layer was separated and dried over Na_2SO_4 . Removal of the ether left a dark residue which was dissolved in petroleum ether, treated with activated charcoal, filtered, concentrated, and cooled to afford white crystals (600 mg), shown by melting point and infrared spectrum to be $(\text{CH}_3)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$. The mother liquor again contained $(\text{CH}_3)_2\text{Sn}(\text{C}_6\text{F}_5)_2$.

CHAPTER V

ALKYL- AND ARYLTHIOTIN DERIVATIVES

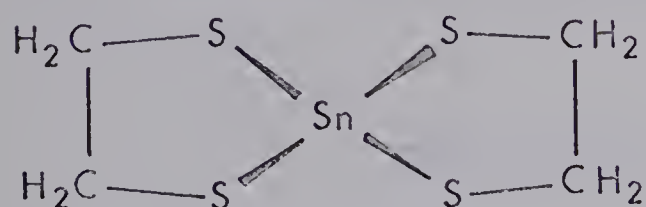
This chapter describes an extensive study of one aspect of the chemistry of compounds containing Sn-Mn and Sn-Re bonds. Here, as in Chapter IV, interest is focused to a greater extent upon the chemistry of the tin atom; that is, the effect of placing various groups on tin and observing marked changes, if any, in gross chemical properties and in the effect upon the metal carbonyl group.

The extensive literature of the organosulfur chemistry of the Group IV metals was reviewed by Ingram, Rosenberg and Gilman (1) in 1960 and more recently by Abel and Armitage (94). Sulfide derivatives such as $(\text{CH}_3)_3\text{Sn-S-Sn}(\text{CH}_3)_3$ and $(\text{C}_2\text{H}_5)_3\text{Sn-S-Sn}(\text{C}_2\text{H}_5)_3$ have been known since 1860 (1,94) but modern studies date from the early 1930's in reports by Backer and Kramer (95,96) on the preparation of the alkyl and aryl compounds $\text{Sn}(\text{SR})_4$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7, p\text{-ClC}_6\text{H}_4$ and others). Kramer and Backer (96) also reported the mixed species $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{SC}_6\text{H}_5)_2$ although few additional samples of this type were known until the early 1950's (97,98,99).

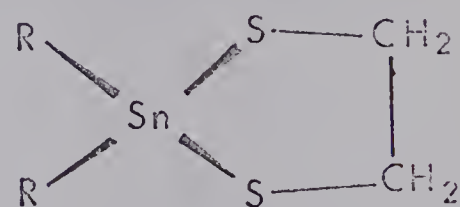
More recently, preparations of compounds of the type $\text{R}_n\text{Sn}(\text{SR}')_{4-n}$ ($\text{R} = \text{alkyl, aryl}$) have been reported

by Abel and Brady (100) and by Davidson et al. (101). Some n-butyltin compounds have been described very recently by Peach (102).

A spiro sulfur-tin system (XI) was first described in 1951 by Backer and Drenth (103). Various mixed systems (XII) have been reported since (100,101,104).

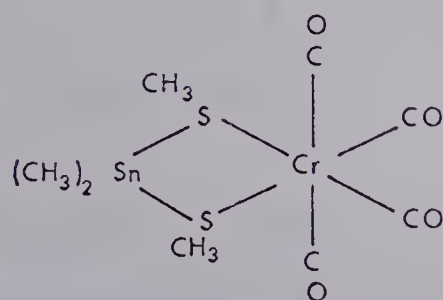


XI



XII

Examples of thiotin systems involving transition metals are few. Abel and Crosse (94) found that $(\text{CH}_3)_2\text{Sn}(\text{SCH}_3)_2$ reacted with $\text{Cr}(\text{CO})_6$ to give a compound in which the sulfur atoms were chelated to the transition metal (XIII). Abel and coworkers also found that metal



XIII

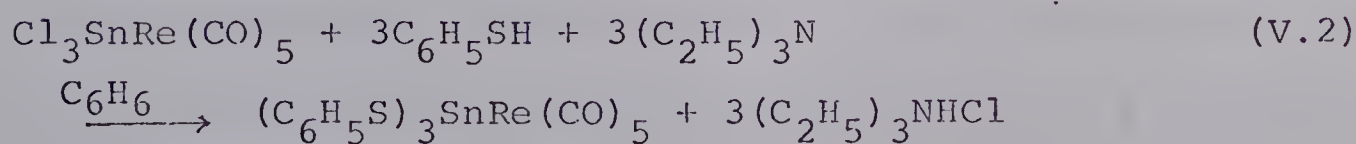
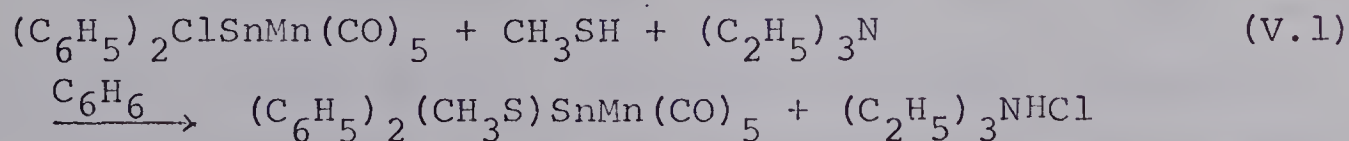
carbonyl halides such as $M(\text{CO})_5\text{Br}$ ($M = \text{Mn}, \text{Re}$) will react with $\text{R}_2\text{Sn}(\text{SR})_2$ to give polymeric species $[\text{M}(\text{CO})_3\text{SR}]_n$ ($n = 3$ or 4) plus the alkyl tin bromide (105).

This chapter describes the preparation of the first thiotin compounds in which there is a direct tin-transition metal bond. Infrared studies are discussed in Chapter VII. Nmr spectra of the CH_3S derivatives are discussed in Chapter VIII.

RESULTS AND DISCUSSION

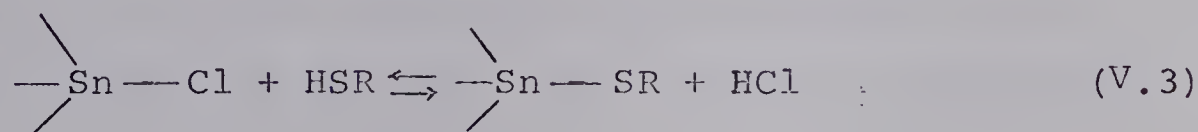
a. Non-Cyclic Systems

All of the seventeen non-cyclic, monomeric compounds prepared in this work were synthesized by the same route. This involved a method first used by Wieber and Schmidt (104) in which a tin halide is stirred with a thiol, RSH ($\text{R} = \text{C}_6\text{H}_5, \text{CH}_3, \text{C}_6\text{F}_5$), in an organic solvent (usually benzene) in the presence of an organic base such as triethylamine or pyridine. Reactions proceeded according to equations, V.1 and V.2.



A variation on this procedure introduced by Abel and coworkers (100,106) utilizes an aqueous system, with hydroxide as the base. Good yields were obtained but the reaction was dependent upon the tin halide having a degree of solubility in water.

The reactions of the thiols with $R_nCl_{3-n}SnM(CO)_5$ ($R = CH_3, C_6H_5$; $M = Re, Mn, n=1,2$) in the presence of triethylamine were immediate and readily apparent. No visible change occurred when the first two components were mixed. However, addition of the amine resulted in the formation of a bright yellow to amber solution containing a fine suspension of the hydrochloride salt of the amine. It is possible that this reaction involves an equilibrium between the thiol and the halide (equation V.3). Addition of the amine removes the HCl causing the

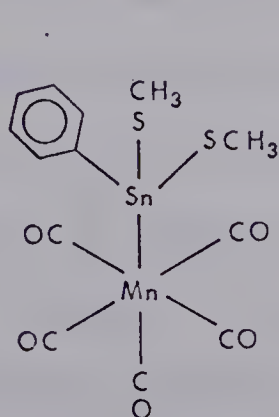


equilibrium to shift to the right forming the product.

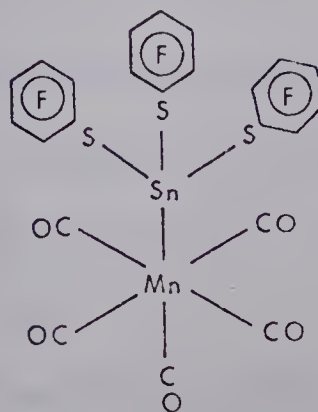
An alternative but less probable reaction route could be one in which the RS^- anion is produced by reaction of the thiol and amine since the S-H bond is somewhat acidic. The thiophenoxide or thioalkoxide ion would then react with the tin halide causing halide displacement and precipitation of the hydrochloride salt.

Yields of the thio derivatives obtained by the Wieber and Schmidt reaction varied widely as may be seen from Table VII. Reduced yields in some cases were most probably due to formation of polymeric materials, which appeared as colored oils with the reaction product. The composition of these oils is unknown. Purification of the products was often difficult because the oils tended to contaminate the crystalline products. A second factor tending to decrease yields was the great solubility of the thiotin-metal carbonyl derivatives even in petroleum ether. In two cases, it was necessary to cool the solution to -78° to induce crystallization and then decant the supernatant liquid before appreciable warming occurred.

The structure of these compounds is presumed to involve octahedral manganese and tetrahedral tin as shown in XIV and XV below. The bulkier organosulfur



XIV



XV

group might be expected to affect the ease with which nicely crystalline products could be obtained, as was indeed the case, especially for $(C_6F_5S)_3SnMn(CO)_5$. The non-cyclic compounds varied in color from white to bright yellow with the color intensity increasing as the number of RS groups increased in any given series.

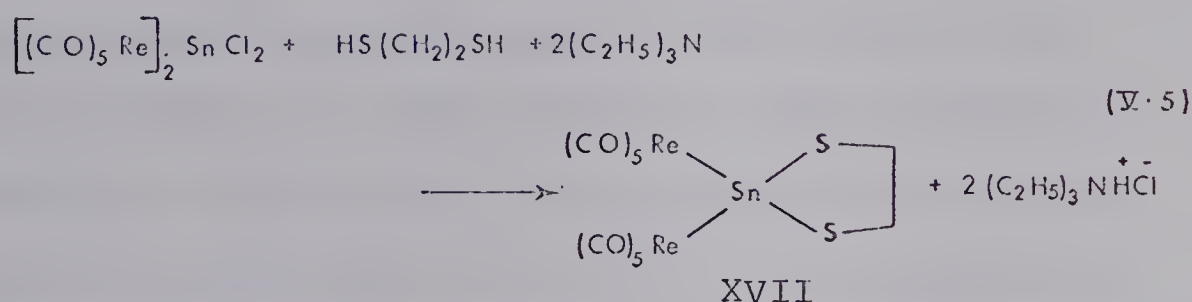
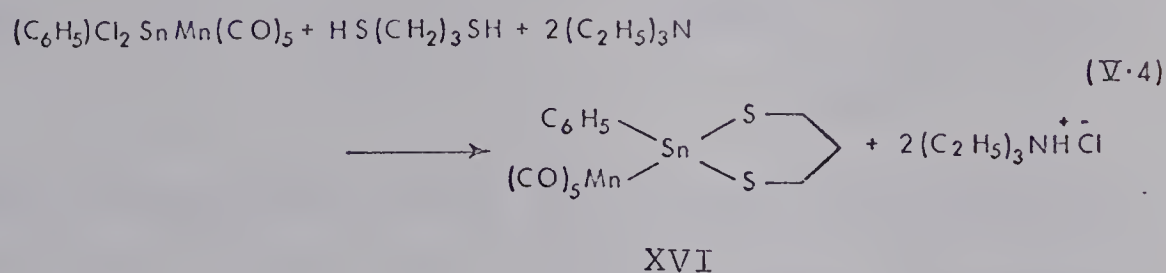
In the solid state, the non-cyclic systems are for the most part moderately stable to light and air. Exceptions to this rule were CH_3S and C_6H_5S derivatives of $(CH_3)_2ClSnMn(CO)_5$ which were liquid at room temperature. The CH_3S - derivative could not be isolated in a pure state due to its tendency to decompose within a few minutes. In solution, stability of this compound was such that an nmr spectrum could not be obtained. The solid methylthio derivatives of the series have shown a tendency to turn green over a period of months.

b. Heterocyclic Derivatives

As mentioned in the introduction, cyclic tin-sulfur compounds have been known since 1951 (104). In the present work heterocycles containing $Mn(CO)_5$ and $Re(CO)_5$ bonded to tin were prepared in order to observe the effect of reducing the symmetry of the molecule on the carbonyl stretching pattern (Chapter VII).

The seven compounds obtained from ethanedithiol,

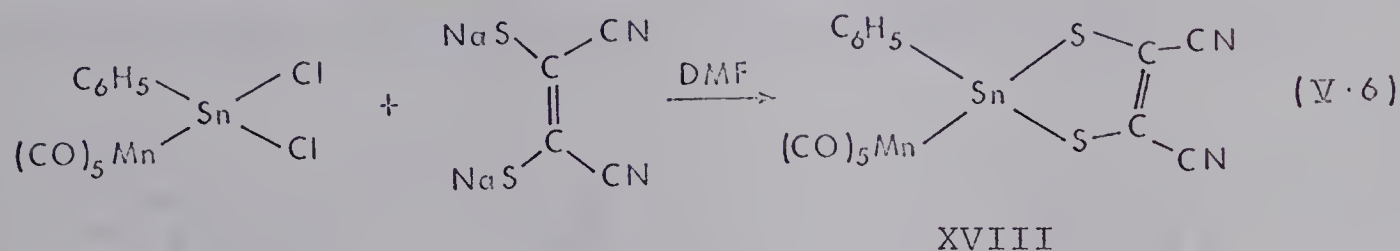
propane-1,2- and 1,3-dithiol were prepared using the halide-thiol-amine combination. Reaction of the first two components in stoichiometric amounts with a slight excess of triethylamine gave the beautifully crystalline yellow solids in moderate to good yields (equations V.4 and V.5). The intense yellow coloration in these



compounds, and to a lesser extent in the straight-chain series, could be a result of greater electron delocalization through the S-Sn-Mn system. It is to be noted that derivatives not containing metal carbonyl groups are all white. Further aspects of the bonding are discussed in Chapter VII.

Preparation of the unsaturated ring system (XVIII) presented a few problems. The principle one was that the starting material, disodium maleonitrile dithiolate, is soluble only in polar media such as alcohols, di-

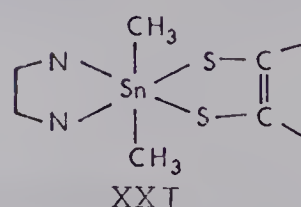
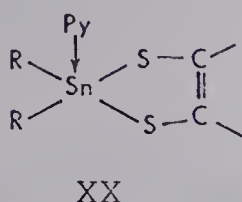
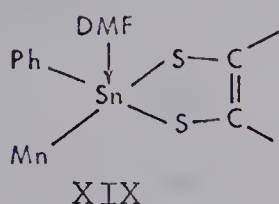
methyl formamide (DMF), dimethylsulfoxide (DMSO) and water. After two test reactions, DMF was chosen and found to be satisfactory. The reaction proceeded as shown in equation V.6.



The properties of this derivative were strikingly different from those with saturated rings. The yellow crystalline solid was insoluble in hydrocarbon solvents and was finally recrystallized in good yield by slow addition of water to a DMF solution. The insolubility is probably a consequence of the polar nitrile groups. In accord with its polar character, this compound decomposed at temperatures above 200° whereas the saturated ring derivatives all had sharp melting points from 79° to 160°.

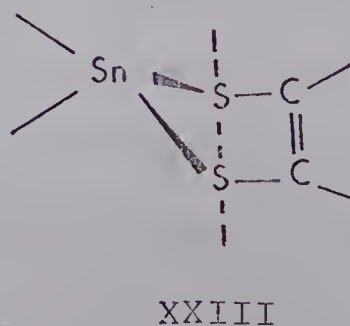
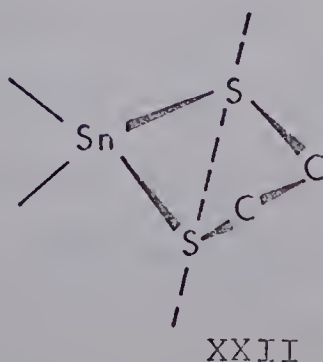
There was some evidence to suggest that the material as obtained from DMF-H₂O solutions contained tin in a higher coordination state than four. Some of the crystals used for melting point determinations became opaque at temperatures of 130° to 140° possibly indicating that solvent of crystallization was being lost.

Some weight loss occurred when a sample was heated at 56° under vacuum and after this treatment a melting point determination indicated no loss of solvent at 130-140°. A higher coordination state would result if complexes of DMF were formed as shown in XIX. A similar type of compound (XX) was isolated by Abel and



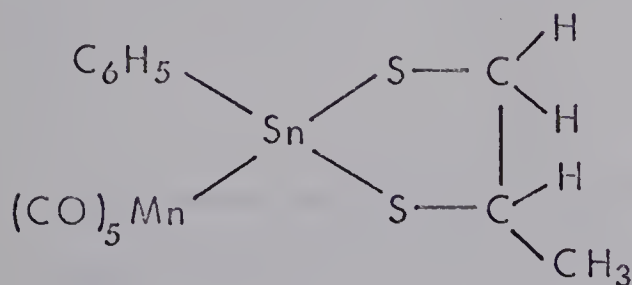
Jenkins (107); in the case where pyridine was adducted, easy loss of the base at reduced pressures occurred. Use of o-phenanthroline resulted in a stable 1:1 complex (XXI) containing 6-coordinate tin.

A structural study of $\text{ClSbS}(\text{CH}_2)_2\text{S}$ (108) has shown that the ring XXII is not planar but that the carbon-carbon single bond is skewed and that there is a fold about the S-S axis. However, Abel points out that the carbon and sulfur atoms in XXIII are necessarily coplanar because of the double bond; any non-planarity

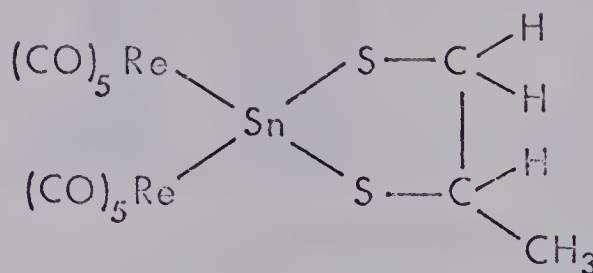


being restricted to a folding about the S-S axis.

The two derivatives of propane-1,2-dithiol require special mention. As structure XXIV shows, there arises the possibility of geometrical isomers.



XXIV



XXV

If, for simplicity, the dithiacyclopentane system is considered to be planar, the phenyl and $\text{Mn}(\text{CO})_5$ groups lie above and below the plane of the ring. Isomers will arise depending upon whether the ring methyl group is cis or trans to the metal carbonyl. On the other hand, no isomers will arise in XXV because the other groups attached to tin are identical. No attempt was made to isolate the two isomers of XXIV although they were observed in the nmr spectrum. Figure 1 shows the nmr spectrum of propane-1,2-dithiol; in the methyl region two peaks due to splitting by the single methine C-H are observed. A spectrum very similar to this is observed in Figure 2 for the compound XXV. However, for the unsymmetrical case (Figure 3), four resonance peaks are observed of which one pair may be attributed to each isomer. The methyl group, of course, exists in slightly

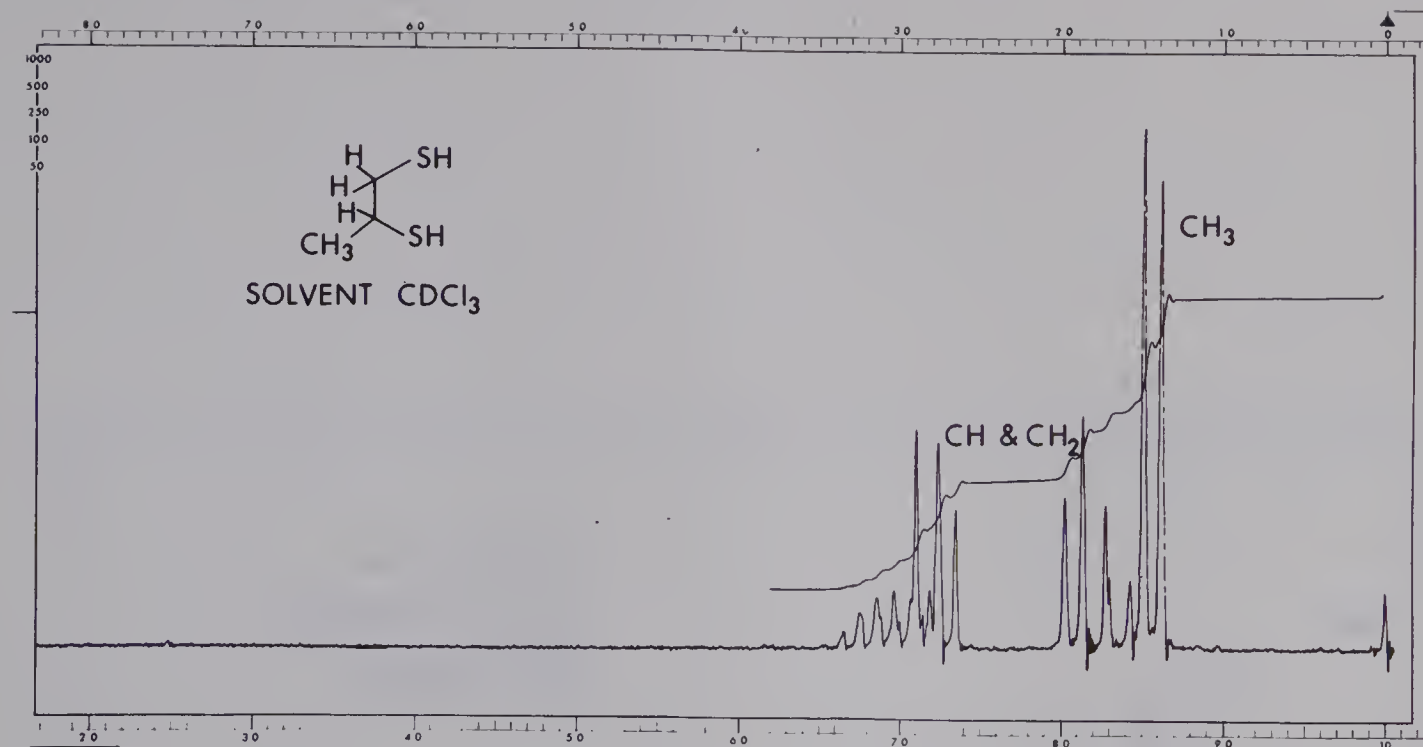


FIGURE 1

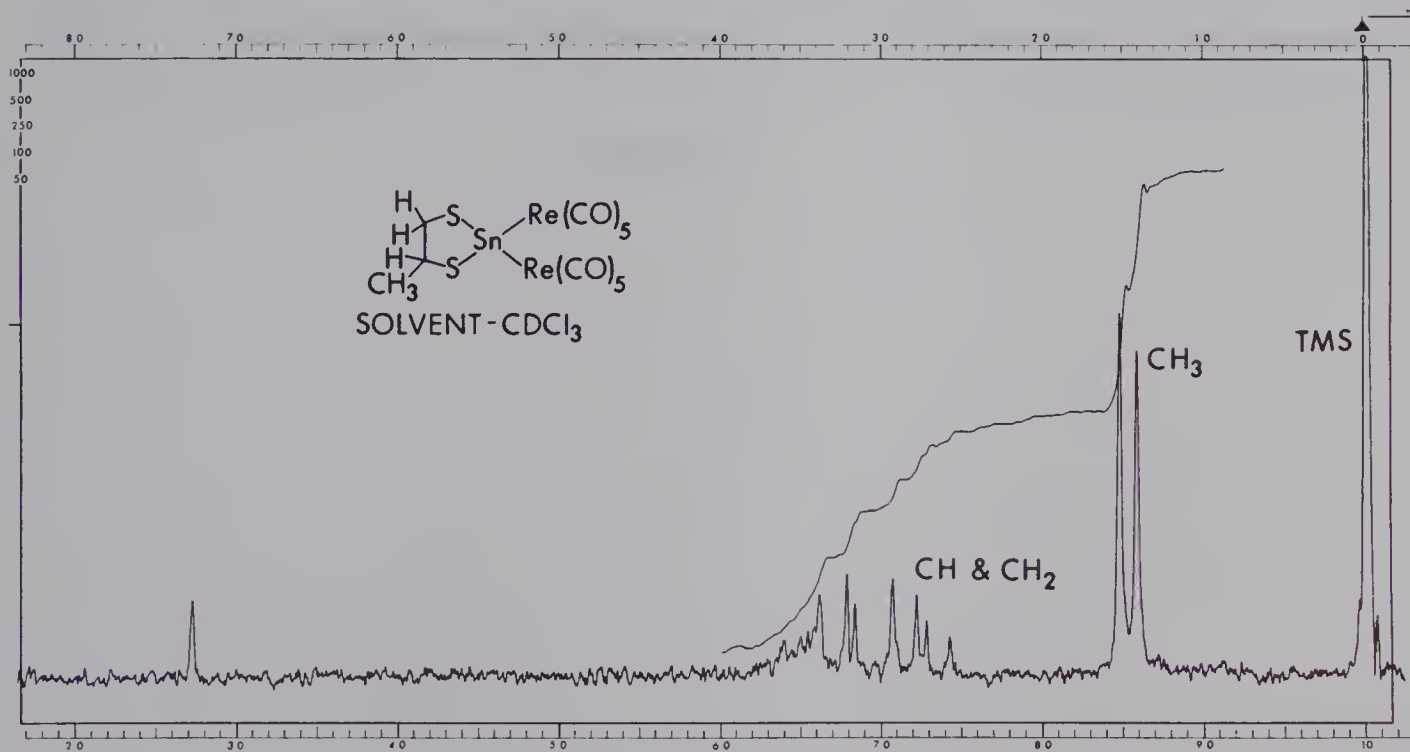


FIGURE 2

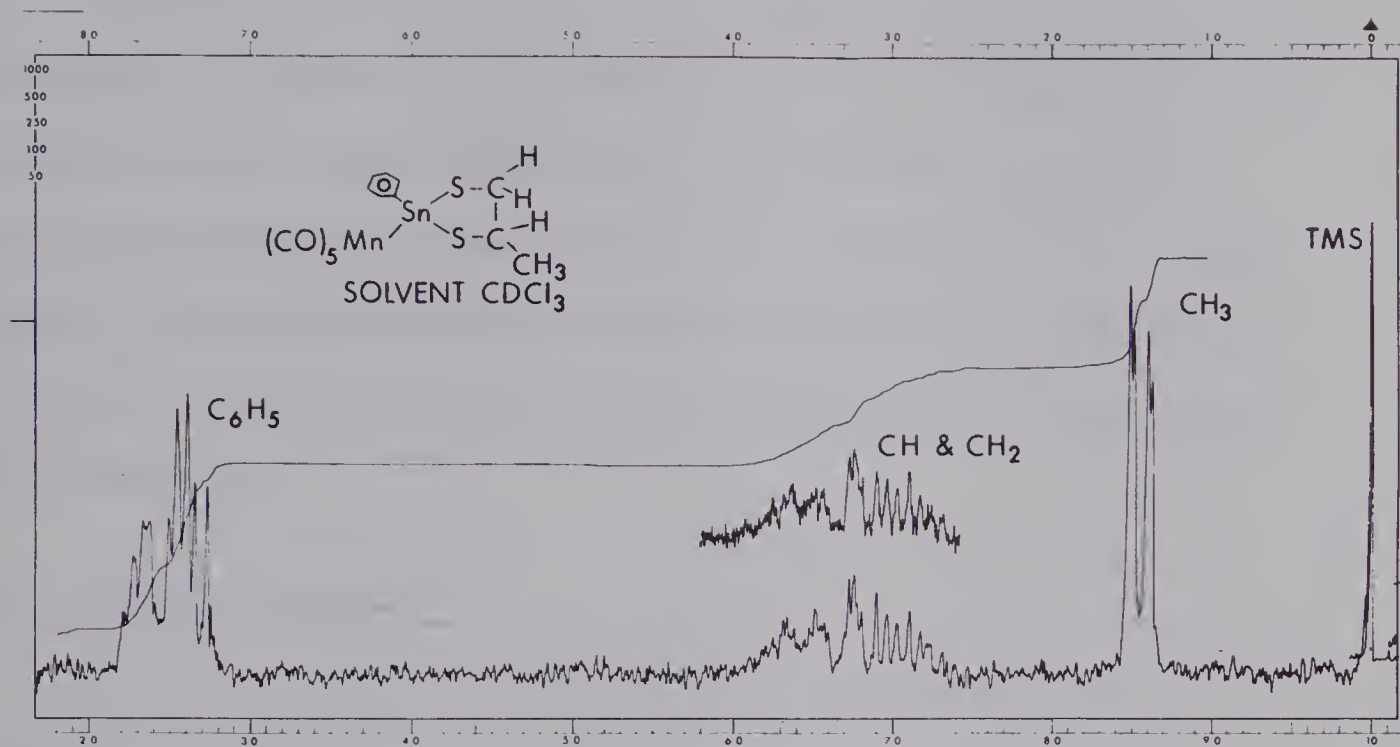


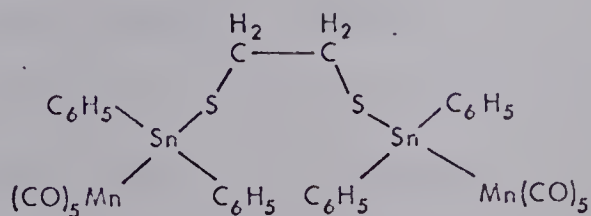
FIGURE 3

different electronic environments in the two isomers. Assignment of the peaks to the isomers would require a more rigorous study of the system.

A similar phenomenon was noted for the methylene protons of ethanedithiol derivatives. If the other two groups on tin were identical (e.g. $\text{Mn}(\text{CO})_5$) only one sharp CH_2 resonance was observed. Substitution of one $\text{Mn}(\text{CO})_5$ with phenyl or chlorine resulted in a multiplet indicating that the CH_2 protons were again in different environments.

c. Bridged Systems

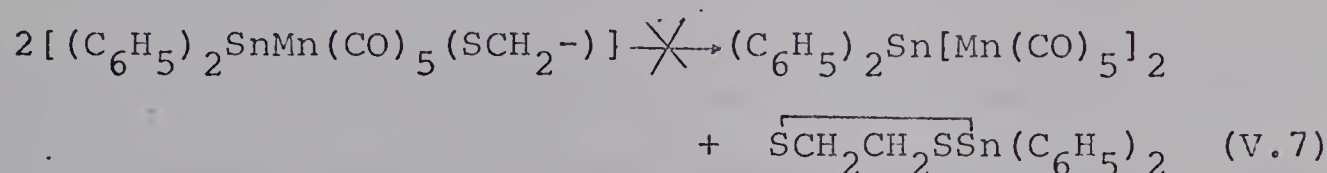
Some of the new derivatives synthesized in the present work contain two tin atoms connected by one or two bridging sulfur atoms and in one case by the $-\text{S}(\text{CH}_2)_2\text{S}-$ group. This latter compound (XXVI) was prepared by the reaction of two moles of $(\text{C}_6\text{H}_5)_2\text{ClSnMn}(\text{CO})_5$ with one mole of the dithiol in the presence of two moles of triethylamine. The compound is a stable white crystal-



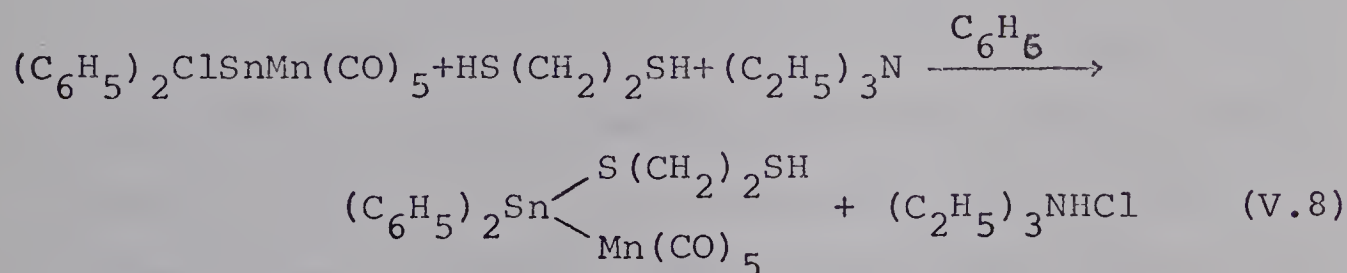
XXVI

line solid easily obtainable from hydrocarbon solution.

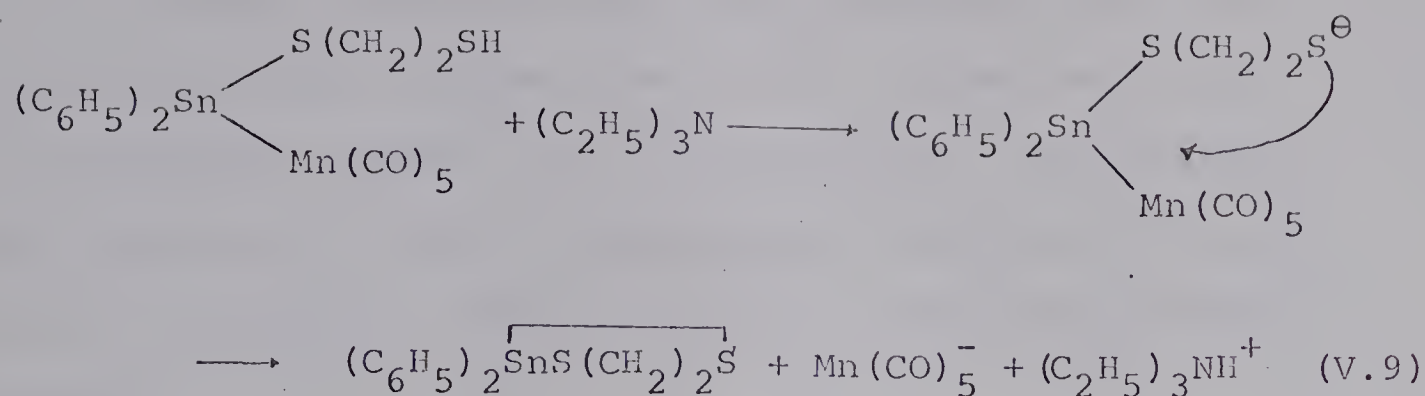
Obtained as by-products of the reaction were the known compounds $(C_6H_5)_2Sn[Mn(CO)_5]_2$ and $\overline{S(CH_2)_2SSn(C_6H_5)_2}$ which no doubt occurred as redistribution products. However, it cannot be concluded that they result from rearrangement of the bridged product (equation V.7), since, once obtained, it was stable in solution with no tendency



to disproportionation. It is possible that there is a competing reaction in which the organo-sulfur ligand is chelating to the tin. In either reaction the first step is probably:



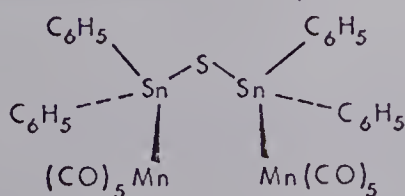
Then as a second step, two reactions could be possible; one would be the bridging reaction, the other one in which the remaining thiolic proton is abstracted and the charged 'end' attacks the tin as in equation V.9.



The Mn(CO)_5^- anion could then react with another molecule of starting material to give the bis-metal carbonyl compound (equation V.10).



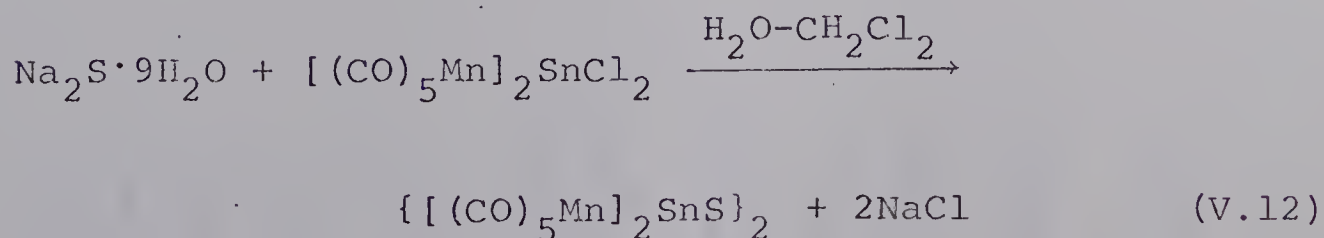
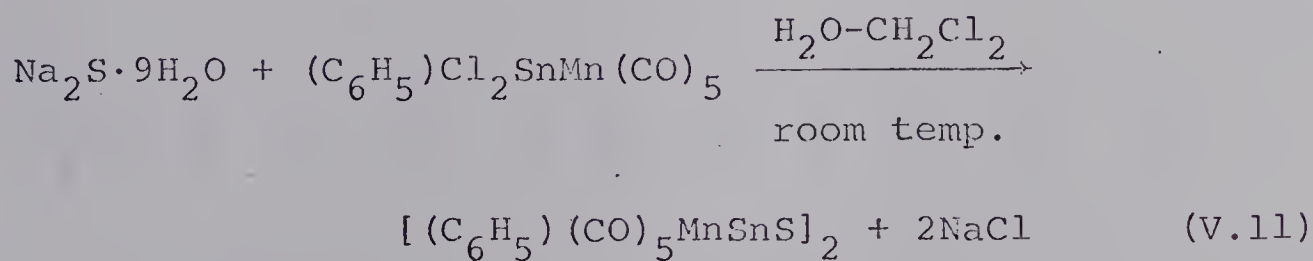
The compound having a single sulfur bridge (XXVII) was obtained by passing gaseous hydrogen sulfide through a benzene solution of $(\text{C}_6\text{H}_5)_2\text{ClSnMn(CO)}_5$ and triethylamine. The product was a stable, white crystalline solid readily soluble in organic solvents and exhibiting the usual slow decomposition in solution.



XXVII

A similar reaction with $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ did not yield the sulfur bridged species but instead only the rearrangement product, $(\text{CH}_3)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$, was obtained. The coproduct of such a rearrangement would be $(\text{CH}_3)_2\text{SnS}$, which is known as a trimer (1,94); it was not detected, however.

The two compounds having twin sulfur bridges were obtained by a novel reaction which was reported recently by Midgal et al. (109) for the preparation of organotin sulfides. This involved an interfacial reaction in which solutions of the reactants in immiscible solvents were stirred together for about two hours. In the two preparations in this work, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was dissolved in a small volume of water and stirred with the appropriate halotin species dissolved in methylene chloride (equations V.11 and V.12). The two derivatives exhibited a high



degree of inertness. Both decompose without melting at temperatures approaching 200° , and both are insoluble

TABLE VI

SUMMARY OF PREPARATIONS OF ALKYL- AND ARYLTHIOTIN DERIVATIVES

Compound	Amount of Reagent Used			Recryst ⁿ Solvent ^a	Remarks	% Yield
	Halide(g)	Thiol(cc)	Amine(cc)			
(PhS) ₃ SnMn(CO) ₅ ^b	0.84	0.62	0.83	A		43
(MeS) ₃ SnMn(CO) ₅	0.84	Excess	0.83	B(-78°)	Mother liquor decanted from crystals.	
(PhS) ₃ SnRe(CO) ₅	0.83	0.47	0.63	A	Product forms as long needles.	44
(MeS) ₃ SnRe(CO) ₅	0.83	Excess	0.65	B	Mixture warmed to 50° to induce reaction.	67
(PhS) ₂ Sn[Mn(CO) ₅] ₂	0.96	0.41	0.56	B(-78°)		53
(MeS) ₂ Sn[Mn(CO) ₅] ₂	0.96	Excess	0.56	A	Crystals form as plates.	63
(MeS) ₂ Sn[Re(CO) ₅] ₂	0.84	Excess	0.28	B	Mixture warmed to induce reaction.	75
MeSSn[Mn(CO) ₅] ₃	0.74	Excess	0.14	C	Reaction mixture dark green.	27
Ph ₂ (MeS)SnMn(CO) ₅	0.76	Excess	0.21	B(-78°)	Dark green reaction mixture.	39
Ph ₂ (PhS)SnMn(CO) ₅	0.76	0.16	0.22	B	See Experimental Section for complete description.	88
Ph(MeS) ₂ SnMn(CO) ₅	0.92	Excess	0.56	A	Polymeric by-product difficult to separate. Accomplished by addition of hexane to crude reaction product	Low

TABLE VI (continued)

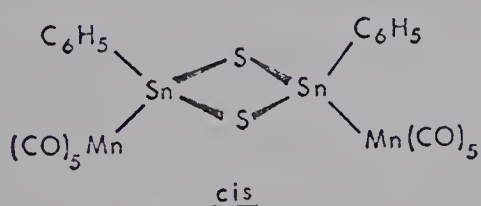
Compound	Amount of Reagent Used			Recryst ⁿ Solvent	Remarks	% Yield
	Halide(g)	Thiol(cc)	Amine(cc)			
$\text{Ph(PhS)}_2\text{SnMn(CO)}_5$	0.92	0.41	0.56	B	Product obtained by decanting mother-liquor and drying under N_2 .	62
$\text{Me}_2(\text{PFS})\text{SnMn(CO)}_5$	0.76	0.26	0.28	B	Product darkened over 2-day period.	27
$\text{Ph}_2(\text{PFS})\text{SnMn(CO)}_5$	0.76	0.20	0.22	A		77
$\text{Ph(PFS)}_2\text{SnMn(CO)}_5$	0.92	0.52	0.56	A	Long yellow needles.	59
$\text{S(CH}_2)_2\text{SSnMn(CO)}_5$ Ph	0.6	0.11	0.36	A		53
$\text{S(CH}_2)_2\text{SSnMn(CO)}_5$ Cl	0.84	0.17	0.55	A		51
$\text{S(CH)}_3\text{SSnMn(CO)}_5$ Ph	0.92	0.2	0.56	D	Specific gravity of thiol = 1.08.	<20
$\text{SCH(CH}_3)_2\text{CH}_2\text{SSnMn(CO)}_5$	0.92	0.21	0.56	A		40
$\text{SCH(CH}_3)_2\text{CH}_2\text{SSn[Re(CO)}_5\text{]}_2$	0.6	0.1	0.3	E	Yellow plates or needles.	85

a. A = hexane; B = petroleum ether; C = acetone-water; D = methanol; E = methylene chloride-petroleum ether.

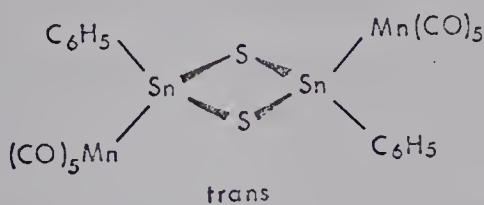
b. All reactions carried out in benzene (15-25 ml) at room temperature unless otherwise indicated. $\text{Cl}_3\text{SnMn(CO)}_5$ and $\text{Cl}_3\text{SnRe(CO)}_5$ used as suspensions in benzene.

in most solvents. The phenyl derivative dissolved in warm methylene chloride and was obtained as pale yellow crystals by addition of petroleum ether. The bis-Mn(CO)₅ compound, however, was extremely insoluble, and precipitated during the reaction in an analytically pure state.

Although the phenyl compound can exist in principle as cis and trans isomers (XXVIII and XXIX) only one form was isolated; this was tentatively assigned the trans structure (XXIX) using infrared criteria to be discussed in Chapter VII. A trace amount of a yellow impurity in the crude sample may possibly have been the cis form.



XXVIII



XXIX

EXPERIMENTAL SECTION

Analyses, melting points, molecular weights and exact masses were obtained as described in Chapter II.

The halo-tin starting materials were prepared according to procedures in Chapters II and III. The mercaptans, ethanedithiol, propane-1,2-dithiol and propane-1,3-dithiol were obtained from Aldrich Chemical Co. Inc. Milwaukee, Wisconsin. Benzenethiol, methanethiol

and hydrogen sulfide were supplied by the Matheson Coleman and Bell Co. of Norwood, Ohio and the Matheson Co. of Whitby, Ontario. Disodium maleonitrile dithiolate was prepared from sodium cyanodithioformate according to the method of Bahr and Schleitzer (110, 111).

All reactions were carried out in the fume hood because of the stench of the thiols. The liquid thiols and triethylamine were measured by means of a syringe in all cases. Reactions were done under a nitrogen atmosphere, although this precaution may not have been required.

Except for minor variations in reaction times and work-up procedures, most of the compounds reported in this chapter were prepared by the same method. Accordingly, only those compounds for which major differences in preparation and work-up were involved will be discussed in detail. For the remainder, one detailed description is given and the rest are shown in Table VI.

Diphenyl(phenylthio)(pentacarbonylmanganese)tin(IV),

$(C_6H_5)_2(C_6H_5S)SnMn(CO)_5$:

To a benzene solution (20 ml) of $(C_6H_5)_2ClSnMn(CO)_5$ (0.76 g, 1.5 mmoles) was added 0.16 cc (1.5 mmoles, sp. gr. 1.57) of benzenethiol and 0.22 cc (1.5 mmoles, 10% excess, sp gr 0.73) of $(C_2H_5)_3N$. The reaction mixture became yellow immediately and a fine, white solid was precipitated. After stirring for 0.5 hr the mixture was filtered on a sintered glass funnel. Removal of solvent

at reduced pressure provided a yellow oil which was subsequently dissolved in petroleum ether. A second filtration to remove dark impurities was followed by concentration and cooling for several hours at -78° to give 680 mg of pale orange crystals. A second crystallization from the same solvent produced shiny white crystals (500 mg) of the product.

Preparations of compounds not listed in Table VI are given in the following descriptions.

Dimethyl(phenylthio)(pentacarbonylmanganese)tin (IV),
 $(\text{CH}_3)_2(\text{C}_6\text{H}_5\text{S})\text{SnMn}(\text{CO})_5$

To a solution of 0.76 g (2 mmoles) of $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ in 20 ml of benzene were added 0.21 cc (2 mmoles) of $\text{C}_6\text{H}_5\text{SH}$ and 0.28 cc (2 mmoles plus a slight excess) of $(\text{C}_2\text{H}_5)_3\text{N}$. After stirring for about 15 minutes, the precipitated $(\text{C}_2\text{H}_5)_3\text{NHCl}$ was removed by filtration and the solvent removed at reduced pressure. An oil that was extremely soluble in petroleum ether was obtained. Cooling a concentrated solution of the oil to -78° (Dry-ice-acetone) gave pale yellow crystals which could be isolated only by decanting the cold, supernatant liquid and pumping the crystals dry under vacuum for a few hours. The crystals melted near room temperature.

In a similar reaction an attempt was made to prepare $(\text{CH}_3)_2(\text{CH}_3\text{S})\text{SnMn}(\text{CO})_5$. Gaseous CH_3SH was

bubbled into a benzene solution (20 ml) of 2 mmoles of $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ while 0.28 cc of $(\text{C}_2\text{H}_5)_3\text{N}$ was added. After 15 minutes, the amine hydrochloride was removed by filtration and solvent removed to give a yellow oil containing some solid impurity. The oil was dissolved in petroleum ether, filtered and cooled to -78° . White crystals of the product were obtained from the solution at this temperature but on warming melted to give an oil containing more solid impurities. An analytical sample of this compound could not be prepared but an infrared spectrum in cyclohexane solution did show bands at 2093, 2025, 2005 and 1997 cm^{-1} in a pattern characteristic of $\text{Mn}(\text{CO})_5$ derivatives (see Chapter VII).

Reaction of $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ with H_2S :-

Gaseous H_2S from a lecture bottle was bubbled into a solution of 0.76 g (2 mmoles) of $(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$ in 20 ml of benzene. Upon addition of 0.28 cc (2 mmoles) of triethylamine, a pale yellow color and a white precipitate formed. After the mixture had stirred for about 10 minutes the color had deepened to orange. Filtration by suction and removal of solvent at reduced pressure provided a brown solid which was dissolved in benzene and petroleum ether added. A dark red oil was deposited and the clear, yellow supernatant liquid decanted. Removal of solvent gave a yellow crystalline

material which was identified as $(\text{CH}_3)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ by its melting point (Table IV), infrared and nmr spectra (Chapters VII and VIII).

In another reaction, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in slight excess and ethyl alcohol were used. Again, the only identifiable product was $(\text{CH}_3)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$.

Reaction of $\text{HS}(\text{CH}_2)_2\text{SH}$ with $(\text{C}_6\text{H}_5)_2\text{ClSnMn}(\text{CO})_5$:

To 1.0 g (2 mmoles) of $(\text{C}_6\text{H}_5)_2\text{ClSnMn}(\text{CO})_5$ in 30 ml of benzene was added 0.09 cc (1 mmole plus a slight excess) of ethanedithiol (sp gr 1.12) and 0.28 cc of triethylamine. The colorless solution immediately became amber and the amine hydrochloride precipitated. The mixture was stirred for 15 minutes at room temperature and filtered. Solvent was removed at reduced pressure from the filtrate, leaving an amber oil, most of which dissolved in warm petroleum ether. After filtration, this solution was cooled, affording white needles (190 mg). This material showed only a very weak absorption in the terminal carbonyl stretching region. Comparison of its nmr spectrum and melting point with an authentic sample of $(\text{C}_6\text{H}_5)_2\text{SnS}(\text{CH}_2)_2\text{S}$ (112) showed them to be identical. The authentic sample gave proton signals at 2.2-2.8 (C_6H_5) and at τ 6.8 (CH_2) integrating in the ratio of $2\frac{1}{2}:1$. The material obtained in this reaction (after recrystallization from hexane to remove the carbonyl-containing impurity) showed identical chemical

shift values and integrated in a ratio of 3:1. The melting point of the authentic sample was 110-112°, this reaction product melted at 106-110°.

The petroleum ether mother liquor was taken to dryness to give a brown solid. An infrared spectrum indicated a probable mixture. Dissolution of the solid in the minimum amount of petroleum ether and slow cooling of the solution gave white crystals of $[(C_6H_5)_2(CO)_5MnSnSCH_2-]_2$. Nmr proton shifts were observed at τ (2.2-2.75) and τ 7.40, integrating in the ratio of 5:1.

The remaining component of the mixture was obtained in low yield (~ 20 mg) from the mother liquor. Its infrared spectrum showed it to be $(C_6H_5)_2Sn[Mn(CO)_5]_2$.

Reaction of $(C_6H_5)_2ClSnMn(CO)_5$ with H_2S :

A solution of 0.5 g (1 mmole) of $(C_6H_5)_2ClSnMn(CO)_5$ in 20 ml of benzene was saturated with H_2S and excess $(C_2H_5)_3N$ (0.2 cc) was added (0.14 cc required). The solution became yellow and $(C_2H_5)_3NHCl$ was deposited. After brief stirring at room temperature, the mixture was filtered and stripped of solvent to yield a red-brown, semi-crystalline solid. Extraction with hot hexane and cooling of the clear colorless solution gave white plates (210 mg) of $[(C_6H_5)_2SnMn(CO)_5]_2S$.

Preparation of $\text{SC}(\text{CN})=\text{C}(\text{CN})\text{SSn}(\text{C}_6\text{H}_5)[\text{Mn}(\text{CO})_5]$:-

0.46 g (1 mmole) of $(\text{C}_6\text{H}_5)\text{Cl}_2\text{SnMn}(\text{CO})_5$ in dimethylformamide (DMF, Fisher Certified Reagent, 25 ml) was stirred with 0.2 g (1.1 mmoles) of cis-disodium maleonitrile dithiolate added as a solid. The initially clear solution became cloudy. The mixture was stirred for 1/2 hour and then, with rapid stirring, water was added. The orange precipitate that was deposited was filtered, washed with distilled water and dried in vacuo in a drying pistol with P_2O_5 for 3½ hours at room temperature. 0.42 g of the dry semi-crystalline solid were obtained. Some of the sample was recrystallized from chloroform-petroleum ether to give small, yellow crystals. The remainder was dissolved in a small volume of DMF to which water was added slowly. The yellow needles that were obtained were filtered, washed with water and dried in vacuo over P_2O_5 . On heating some crystals on the Kofler hot stage the presence of some solvent of crystallization was evident (partial melting at 130-140). Treatment of the crystals under high vacuum (0.05 mm) overnight at refluxing acetone temperature removed any trapped solvent.

Tris(pentafluorophenylthio)(pentacarbonylmanganese)tin

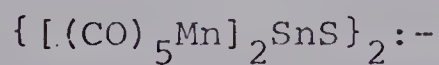
(IV) , $(\text{C}_6\text{F}_5\text{S})_3\text{SnMn}(\text{CO})_5$:-

To a benzene suspension (25 ml) of $\text{Cl}_3\text{SnMn}(\text{CO})_5$ (0.84 g, 2 mmoles) was added 0.77 cc (1.2 g, 6 mmoles) of

$\text{C}_6\text{F}_5\text{SH}$ and (0.83 cc 6 mmoles) of $(\text{C}_2\text{H}_5)_3\text{N}$. The mixture became bright orange and the $\text{Cl}_3\text{SnMn}(\text{CO})_5$ dissolved. After stirring for $\frac{1}{2}$ hour, the amine hydrochloride was filtered off and solvent removed to give a dark, oily residue. After extraction twice with hot hexane, the yellow solution obtained was taken to dryness to give a small amount of yellow solid. This was redissolved in hexane and cooled to give 100 mg of yellow crystals which had a wide melting point range of $120-130^\circ$. Recrystallization from methanol gave lemon yellow crystals of the product in low yield.

In a second attempt, an effort was made to increase the yield. After reaction solvent was removed, the oil was dissolved in methanol and water added slowly to precipitate a bright yellow solid. The weight obtained after drying in vacuo over P_2O_5 was 1.2 g (67%). A recrystallization from the same solvent pair gave finely crystalline material which had infrared spectrum and melting point identical to that for the first sample.

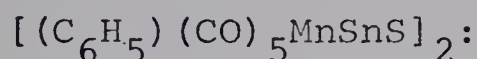
Bis(pentacarbonylmanganese)tin(IV)sulfide Dimer,



0.5 g (0.86 mmole) of $\text{Cl}_2\text{SnMn}(\text{CO})_5]_2$ was dissolved in 15 ml of methylene chloride and stirred in a heterogeneous mixture, with a water solution (5 ml) of 0.21 g

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (0.86 mmole) under nitrogen at room temperature for 2 hours. During this time a bright yellow precipitate formed in the yellow organic layer. The mixture was filtered by suction and the two phases were separated. Removal of solvent from the organic layer afforded 150 mg of an orange solid. The main portion of the product (250 mg) which had precipitated could not be purified by usual chemical means because of its extreme insolubility even in chlorinated solvents. Microscopic investigation indicated the reaction product to be finely crystalline. Analysis (as shown in Table VII) agreed closely with the theoretical values.

Phenyl(pentacarbonylmanganese)tin(IV)Sulfide Dimer



Approximately 500 mg of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 10 ml H_2O was stirred with a methylene chloride solution (15 ml) of 0.92 g (2 mmole) of $\text{C}_6\text{H}_5\text{-Cl}_2\text{SnMn}(\text{CO})_5$ for 2 hours. During this time the CH_2Cl_2 layer became bright yellow.

The immiscible layers were separated and solvent was removed the organic phase after removal of 147 mg of solid by filtration. The solid residue was extracted with hot hexane which yielded 100 mg of yellow material. The remaining solid (450 mg) was dissolved in warm CH_2Cl_2 and petroleum ether added to yield pale yellow crystals

of the product. The other remaining fractions which contained small amounts of an unknown yellow material proved to be the same material as the recrystallized product.

TABLE VII

ANALYTICAL DATA AND PHYSICAL PROPERTIES

Compound	Mp, °C.	Color	Analyses, %									
			Found					Calculated				
			C	H	O	S	C	H	O	S		
(PhS) ₃ SnMn(CO) ₅	98-100	yellow	43.3	2.5	12.6	15.0	43.1	2.4	12.5	15.0		
(MeS) ₃ SnMn(CO) ₅	61-63	pale yellow	23.0	1.9	17.4	20.6	21.1	2.0	17.6	21.1	1	
Me ₂ (PhS)SnMn(CO) ₅ ^a	b	pale yellow	35.8	2.8	17.3	7.0	34.5	2.5	17.7	7.1	108	
Ph ₂ (MeS)SnMn(CO) ₅	71-73	white	41.9	2.7	15.3	6.1	42.0	2.5	15.5	6.2	1	
Ph ₂ (PhS)SnMn(CO) ₅ ^c	93-96	white	47.3	2.7	13.7	4.4	47.9	2.6	13.9	5.6		
Ph(MeS) ₂ SnMn(CO) ₅	42-44	yellow	33.5	2.6	16.6	13.9	32.2	2.3	16.5	13.2		
Ph(PhS) ₂ SnMn(CO) ₅ ^d	63-65	pale yellow	45.4	2.6	13.5	11.5	45.4	2.5	13.1	10.5		
(PhS) ₃ SnRe(CO) ₅	114-117	pale yellow	36.5	1.8	10.3	12.2	35.8	2.0	10.4	12.5		
(MeS) ₃ SnRe(CO) ₅	94-96.5	pale yellow	16.5	1.5	13.6	16.3	16.4	1.6	13.7	16.4		

1
108
1

TABLE VII (continued)

Compound	Mp, °C.	Color	Analyses, %							
			Found				Calculated			
			C	H	O	S	C	H	O	S
(MeS) ₂ Sn[Mn(CO) ₅] ₂ ^e	121-123 dec	bright yellow	24.4	0.9	26.0	12.9	23.9	1.0	26.5	10.6
(PhS) ₂ Sn[Mn(CO) ₅] ₂ ^f	116-119 ^g	bright yellow	37.1	1.4	21.8	8.7	36.4	1.4	22.0	8.8
(MeS) ₂ Sn[Re(CO) ₅] ₂	120-123 dec	yellow- white	16.8	0.4	18.7	7.4	16.7	0.7	18.5	7.4
(MeS)Sn[Mn(CO) ₅] ₃	> 120° dec	orange	25.4	0.5	29.5	4.4	25.6	0.4	32.0	4.3
Me ₂ (Pfs)SnMn(CO) ₅ ^h	87-89	white	28.6	1.2	i	5.8	28.8	1.1	-----	5.9
Ph ₂ (Pfs)SnMn(CO) ₅ ^j	114-117 ^k	pale yellow	41.4	1.6	-----	6.1	41.4	1.5	-----	4.8
Ph(Pfs) ₂ SnMn(CO) ₅ ^l	97-98	yellow	35.4	0.7	-----	6.6	35.0	0.6	-----	8.1
(Pfs) ₃ SnMn(CO) ₅ ^m	164-167 dec	yellow	30.7	0.7	-----	---	30.3	0.0	-----	---
$\overline{\text{S}(\text{CH}_2)_2\text{SSnMn}(\text{CO})_5}$ Ph	121-122	pale yellow	33.0	1.8	-----	---	32.3	1.9	-----	---

TABLE VII (continued)

Compound	Mp, °C.	Color	Analyses, %							
			Found			Calculated				
			C	H	O	S	C	H	O	S
$\overline{\text{S}(\text{CH}_2)_2 \text{SSnMn}(\text{CO})_5}$ Cl	116-119	pale yellow	19.1	1.0	17.9	14.7	19.1	0.9	18.1	14.5
$\overline{\text{SCHCH}_2 \text{SSnMn}(\text{CO})_5^n}$ Me Ph	79-81	pale yellow	33.7	2.4	16.3	12.9	33.8	2.2	16.1	12.9
$\overline{\text{S}(\text{CH}_2)_3 \text{SSnMn}(\text{CO})_5}$ Ph	84-86	pale yellow	33.8	2.6	16.1	12.9	33.8	2.2	16.1	12.9
$\overline{\text{SC}=\text{CSSnMn}(\text{CO})_5^o}$ CN CN Ph	> 200 dec	yellow	34.0	1.1	15.1	12.0	33.9	1.0	15.1	12.1
$\overline{\text{S}(\text{CH}_2)_2 \text{SSn}[\text{Mn}(\text{CO})_5]_2^p}$	141-142	bright yellow	24.6	1.3	-----	-----	24.0	0.7	-----	-----
$\overline{\text{S}(\text{CH}_2)_2 \text{SSn}[\text{Re}(\text{CO})_5]_2^q}$	150-152	bright yellow	17.5	0.7	18.4	-----	16.7	0.5	18.5	-----
$\overline{\text{SCHCH}_2 \text{SSn}[\text{Re}(\text{CO})_5]_2}$ Me	158-160	yellow	18.4	0.9	-----	-----	17.8	0.7	-----	-----
$[\text{Ph}_2 \text{SnMn}(\text{CO})_5]_2 \text{S}^r$	160-167 dec	white	42.2	2.4	15.9	4.0	42.2	2.1	16.5	3.3
$[\text{Ph}_2 \text{SnMn}(\text{CO})_5]_2$ SCH ₂ -	134-136	white	42.1	2.7	15.3	6.4	42.1	2.4	15.7	6.3

TABLE VII (continued)

Compound	Mp, °C.	Color	Analyses, %							
			Found				Calculated			
			C	H	O	S	C	H	O	S
$[(\text{CO})_5\text{MnSnS}]_2$ Ph	> 160 dec	pale yellow	31.3	1.0	18.9	7.6	31.3	1.2	18.9	7.6
$\{[(\text{CO})_5\text{Mn}]_2\text{SnS}\}_2$	> 170 dec	yellow	22.1	0.2	29.2	5.7	22.2	0.0	29.6	5.9

a. Mol wt : calculated, 453; found, 438 (in benzene).

b. Liquid at room temperature.

c. Mol wt : calculated, 577; found, 551 (in benzene).

d. Mol wt : calculated, 609; found, 574 (in CH_2Br_2). Mass spectrum showed molecular ion $[\text{}^{12}\text{C}_{23}\text{}^1\text{H}_{15}\text{}^{55}\text{Mn}\text{}^{16}\text{O}_5\text{}^{32}\text{S}\text{}^{120}\text{Sn}]^+$ at mass 604.

f. Mol wt : calculated, 727; found 693 (in benzene).

g. Partial decomposition.

h. Fluorine: calculated, 17.5; found, 17.5.

i. Oxygen cannot be analyzed in presence of fluorine.

j. Fluorine: calculated, 14.2; found, 14.3. Mol wt ; calculated, 667; found, 655 (in benzene).

TABLE VII (continued)

k.	Partial decomposition.			
l.	Fluorine: calculated, 24.1; found, 23.5. Mol wt: calculated, 789; found, 760 (in benzene).			
m.	Fluorine: calculated, 31.3; found, 32.8. Chlorine: calculated, 0.0; found, 0.0.			
n.	Mol wt : calculated, 497; found, 465 (in benzene).			
o.	Nitrogen: calculated, 5.3; found, 5.4. Exact mass of molecular ion $[^{12}\text{C}_{15}^{1}\text{H}_5^{55}\text{Mn}^{14}\text{N}_2^{16}\text{O}_5^{32}\text{S}^{120}\text{Sn}]^+$; calculated: 531.8042; found 531.8041.			
p.	Mol wt : calculated, 601; found, 588.			
q.	Mol wt : calculated, 863; found, 861.			
r.	Manganese: calculated, 11.4; found, 10.6; Tin: calculated, 24.5; found, 23.5.			
s.	Mol wt : calculated, 1028; found, 955 (in benzene).			

CHAPTER VI

PENTAFLUOROPHENYLDIPHENYLPHOSPHINE DERIVATIVES

The four phosphine derivatives described in this chapter were originally prepared because of interest in the ^{19}F nmr spectrum of the C_6F_5 group. Studies in this field were carried out by Dr. M. G. Hogben of this laboratory (113). Although satisfactory nmr spectra could not be determined for these four compounds because of their low solubility, the chemistry of these derivatives proved to be of interest in relation to that of triphenylphosphine derivatives.

In 1959 a compound formulated as $(\text{C}_6\text{H}_5)_3\text{PMn}(\text{CO})_4$ was reported by Hieber and Freyer (114). It was obtained by reaction of the phosphine with $\text{Mn}_2(\text{CO})_{10}$ in p-xylene at 190° and was thought to be monomeric and paramagnetic. However, derivatives of PR_3 where R was C_6H_{11} or OC_6H_5 were dimeric and diamagnetic. The monomeric nature of the $(\text{C}_6\text{H}_5)_3\text{P}$ derivative was generally accepted and in 1964, Osborne and Stiddard (115) reported preparation of the diamagnetic dimer $[(\text{C}_6\text{H}_5)_3\text{PMn}(\text{CO})_4]_2$ by a photochemical reaction. These authors concluded that the reaction conditions determined whether monomer or dimer was formed.

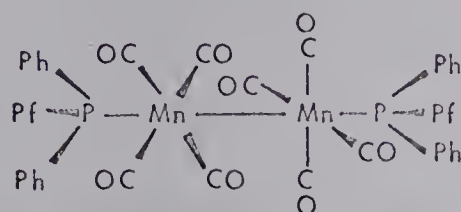
In 1966, Wawersik and Basolo (116) reported that

they were unable to repeat Hieber's preparation of the monomeric, free-radical species. Their results suggested that the Mn-Mn bond did not undergo homolytic cleavage during reaction with $(C_6H_5)_3P$. They did obtain the dimer of Osborne and Stiddard, and also a monosubstituted species $(C_6H_5)_3PMn_2(CO)_9$ which was first reported by Ziegler and coworkers (117) in 1965. Wawersik and Basolo suggested that Hieber had actually obtained the dimer and that the observed paramagnetism may have been due to impurities obtained in the reaction. It is interesting to note, however, that reaction of $(C_6H_5)_3P$ with $Re_2(CO)_{10}$ (118) does provide in addition to the disubstituted compound $[Re(CO)_4P(C_6H_5)_3]_2$, a paramagnetic species which has been formulated as $Re(CO)_3[P(C_6H_5)_3]_2$, with trans phosphine groups in a trigonal bipyramidal geometry.

The only known phosphine-tetracarbonylmanganese derivatives of the R_3Sn group ($R = C_6H_5, Cl$) were reported by Gorsich (19) in 1962. The triphenyltin species could be prepared either by reaction of the $SnMn(CO)_5$ compound with $(C_6H_5)_3P$ at 200° or by reaction of $NaMn(CO)_4P(C_6H_5)_3$ with $(C_6H_5)_3SnCl$. The trichloride was prepared by reaction of chlorine with the triphenyltin derivative.

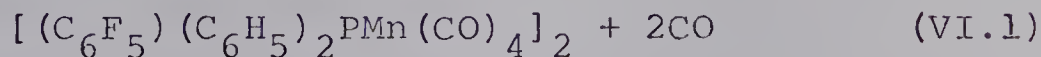
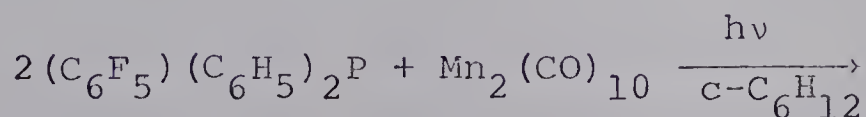
RESULTS AND DISCUSSION

The first phase of this work involved preparation of the dimer $[(C_6F_5)(C_6H_5)_2PMn(CO)_4]_2$ (XXX). It was



XXX

obtained by a photochemical reaction of the phosphine with manganese carbonyl (equation VI.1). Using the apparatus as described in the experimental section it was possible to carry out the reaction near room temperature. Some heating resulted from the quartz lamp

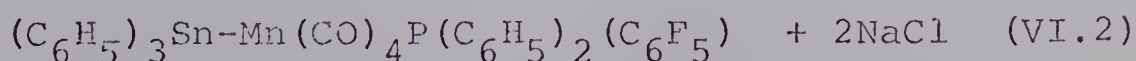
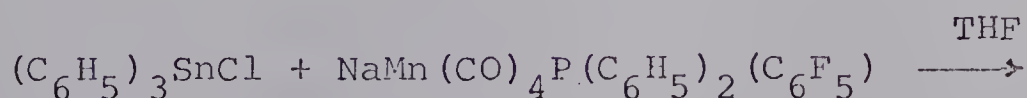


despite water cooling. After an initial reaction period of about two hours it was necessary to remove the heavy precipitate of product which prevented movement of the stirring bar and probably decreased the efficiency of the irradiation. After removal of the initial product, the reaction was continued.

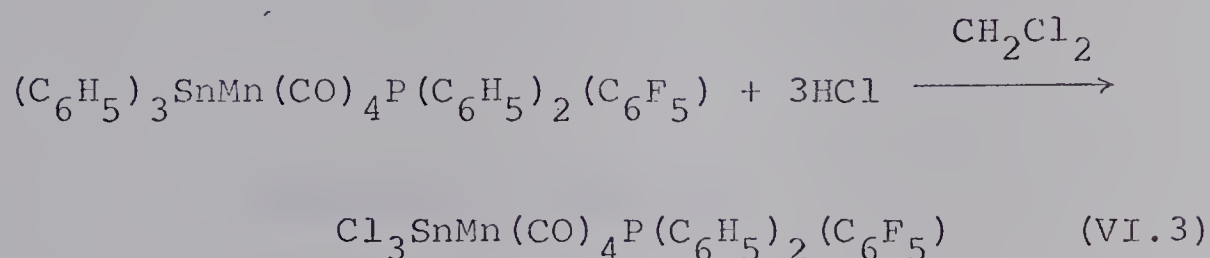
The monosubstituted species $[(C_6F_5)(C_6H_5)_2P]Mn_2(CO)_9$ was isolated in much lower yields as amber crystals. It was easily separable from the disubstituted species due to different solubilities in methanol.

Both species are stable to light and air and decompose only at their melting points. They are appreciably less soluble in organic solvents than the triphenylphosphine analogs (115,117). The disubstituted derivative is quite soluble in CH_2Cl_2 and THF but virtually insoluble in alcohols and hydrocarbons. The nonacarbonyl species was more soluble in alcohols but also quite insoluble in hexane or benzene.

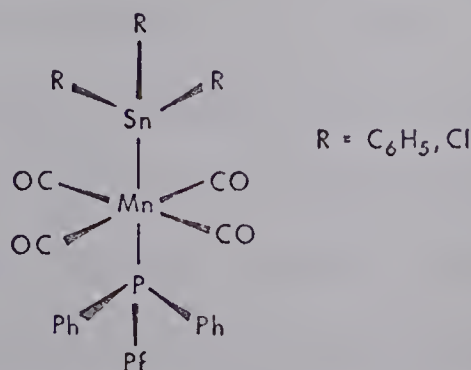
The reaction of the octacarbonyl dimer with 1% sodium amalgam was analogous to that reported by Hieber et al. (119) for the $(C_6H_5)_3P$ derivative. Stirring of a THF solution of the perfluorophenyl analog with sodium amalgam produced a dark red solution; no attempt to isolate the sodium salt was made. Subsequent reaction with $(C_6H_5)_3SnCl$ gave the metal-metal bonded species in good yield (equation VI.2). The cleavage reaction and



and reaction VI.2 were much cleaner than those using $\text{Mn}_2(\text{CO})_{10}$. This is reflected in the yield of the tin complex and is indicative of the stabilizing effect of the phosphine. This effect is also apparent in the reaction of the $(\text{C}_6\text{H}_5)_3\text{Sn}$ - compound with HCl to give nearly quantitative yield of the trichloride (equation VI.3).



Both metal-metal bond derivatives were obtained as nicely crystalline solids. They are presumed to have structures analogous to that found by R. F. Bryan (50) for the triphenyltin compound of Gorsich (19). Infrared evidence for trans-disposition of the tin and phosphine groups (XXXI) is discussed in the following chapter.



XXXI

The solubilities of the $(\text{C}_6\text{H}_5)_3\text{Sn-}$ and $\text{Cl}_3\text{Sn-}$ species continue the trend observed for the mono- and disubstituted carbonyls. They are insoluble in hydro carbons but dissolve readily in polar solvents such as CH_2Cl_2 , acetone and THF. The reduced solubility is probably a consequence of the polar nature of the perfluorophenyl group.

EXPERIMENTAL SECTION

Analyses were carried out as described in Chapter II. Analytical data and physical properties are given in Table VIII.

Preparation of $[(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)_2\text{P}]$

The starting compound perfluorophenyldiphenylphosphine, $[(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)_2\text{P}]$, was obtained using a modification of a procedure developed by Mr. R. S. Gay of this laboratory. It was prepared as follows: 0.1 mole (17.4 g) of $\text{C}_6\text{F}_5\text{Li}$ in 120 ml ether were prepared from $\text{C}_6\text{F}_5\text{Br}$ and $n\text{-C}_4\text{H}_9\text{Li}$ (44 ml of 1.6 M in hexane) as previously described. After stirring for about 4 hours at -78° , 18 g (0.08 mole) of $(\text{C}_6\text{H}_5)_2\text{PCl}$ in 60 ml of ether was added over a period of 1/2 hour. The mixture was allowed to warm to room temperature and stirred overnight. During this time, a white

precipitate had formed in the slightly pink solution. Hydrolysis with 100 ml of water with vigorous stirring (Greiner Heavy Duty motor) resulted in a fine suspension of solid material in the ether layer. The two liquid phases were separated in a separatory funnel and the ethereal layer filtered, dried over MgSO_4 and filtered again to give a clear yellow solution. Solvent was removed to yield a yellow oil which crystallized upon addition of CH_3OH and momentary cooling to -78° . Yield of the white crystalline solid was 20 g (74%); m.p. 71° - 74° .

Reaction of $\text{Mn}_2(\text{CO})_{10}$ with $(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)_2\text{P}$

The apparatus used in this reaction has been used extensively in this research group. It consists of an outer glass cylinder of approximate dimensions 29 cm x 6.5 cm. Fitted by means of a ground glass joint is an inner quartz section with a water cooling jacket. The capacity of the annular space is \sim 150 ml. The UV source rests in the center of the quartz jacket in such a way as to provide maximum irradiation of a solution. The outer cylinder has two extensions which allow use of a condenser and nitrogen bubbler.

In this reaction, the outer cylinder was charged with 150 ml of a cyclohexane (Fisher Certified Reagent)

solution containing 3.9 g (0.01 mole) of $\text{Mn}_2(\text{CO})_{10}$ and 8.84 g (0.05 mole) of $(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)_2\text{P}$. The solution was stirred magnetically (2 inch Teflon bar) and irradiated for an initial period of two hours while nitrogen was bubbled through. During this time a heavy orange precipitate of the disubstituted species $\{[(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)_2\text{P}]\text{Mn}(\text{CO})_4\}_2$ formed. The mixture was filtered and the solid washed with petroleum ether to afford 2 g of a yellow solid. Removal of the cyclohexane from the filtrate left an oil, which was dissolved in methanol and cooled to give crystals of the monosubstituted species, $[(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)_2\text{P}]\text{Mn}_2(\text{CO})_9$. After removal of this product, solvent was removed from the mother liquor and the residue redissolved in 150 ml of cyclohexane. Irradiation for a period of four hours provided an additional 800 mg of the bis-phosphine derivative. This, together with the initial batch, was dissolved in CH_2Cl_2 and methanol was added to give soft orange needles. The nonacarbonyl compound was best recrystallized from ethanol, affording amber needles.

In a subsequent reaction it was found that separation of the two derivatives was facilitated by dissolving the residual oil in CH_2Cl_2 and adding methanol to precipitate the octacarbonyl. The nonacarbonyl species was then

obtained by removal of CH_2Cl_2 after filtration, and recrystallization from methanol.

Preparation of $(\text{C}_6\text{H}_5)_3\text{Sn-Mn}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{F}_5)]$:

A 1% sodium amalgam was prepared from 0.5 g of sodium and 4 ml of mercury. The amalgam was stirred with a solution of the bis-(phosphine)octacarbonyl (2 g, 1.9 mmol) in 50 ml dry THF. The initially cherry-red solution became darker. After stirring magnetically for 80 minutes at room temperature, the amalgam was removed (see Chapter II) and 1.4 g (3.7 mmol) of $(\text{C}_6\text{H}_5)_3\text{SnCl}$ was added. There was an immediate color change to green. The mixture was stirred for 15 minutes at room temperature then filtered to remove a grey precipitate (mainly NaCl). Solvent was removed at reduced pressure leaving an oil which was readily soluble in petroleum ether. Addition of a small amount of this solvent brought about formation of a curdy, gray precipitate. The supernatant liquid was decanted and more petroleum ether added until a cloudiness was noted. Cooling of the solution overnight (-20°) produced 2.4 g (75%) of the product as pale yellow crystals. Recrystallization from CH_2Cl_2 -methanol afforded white plates.

Preparation of $\text{Cl}_3\text{SnMn}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{F}_5)]$:

Anhydrous HCl was bubbled through a methylene chloride solution (25 ml) of the $(\text{C}_6\text{H}_5)_3\text{Sn}$ - derivative (0.9 g, 1 mmole) for 20 minutes; during this time, the color became yellow-green. The solution was stirred for about five minutes after addition of HCl was stopped. Solvent was removed to provide 0.74 g (100%) of a yellow crystalline solid. This was recrystallized from CH_2Cl_2 -petroleum ether to give 640 mg of bright yellow crystals. The color became pale yellow when the material was treated under vacuum at refluxing acetone temperature (56°).

TABLE VIII

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound ^a	Color	Mp. °C	Analyses, %									
			Found					Calculated				
			C	H	P	F		C	H	P	F	
(PFPPh ₂ P)Mn ₂ (CO) ₉	Amber	141-144 dec.	45.4	1.2	5.5	10.4		45.4	1.4	4.3	13.3	1
(PFPPh ₂ P) ₂ Mn ₂ (CO) ₈	Orange	149-150 dec.	50.6	2.0	5.0	19.5		50.8	1.9	6.2	18.2	123
Ph ₃ SnMn(CO) ₄ (PPh ₂ Pf)	White	193-195 dec.	55.4	2.9	3.1	10.1		55.3	2.9	3.6	10.9	1
Cl ₃ SnMn(CO) ₄ (PPh ₂ Pf) ^b	Pale Yellow	174-176 dec.	35.9	1.2	4.0	----		35.5	1.4	4.2	----	

a. Pf represents C₆F₅

b. Cl analysis: Calculated, 14.3; found, 14.8

CHAPTER VII

INFRARED STUDIES

Of all physical methods available, infrared spectrometry is the most widely used by the metal carbonyl chemist. It has enabled him to gain a clearer and more complete picture of the chemical nature of the compounds and of their structures. In this chapter, qualitative infrared studies on the compounds prepared in this work are described and discussed in the light of presently accepted theory.

INTRODUCTION

a. The Metal-Carbon Bond

Transition metals (i.e. those possessing vacant d-orbitals) have the property of being able to form stable complexes with carbon monoxide, which serves to stabilize the metal in a low oxidation state. The stabilizing power is associated with the fact that the donor atom (carbon) possesses vacant orbitals in addition to lone pairs.

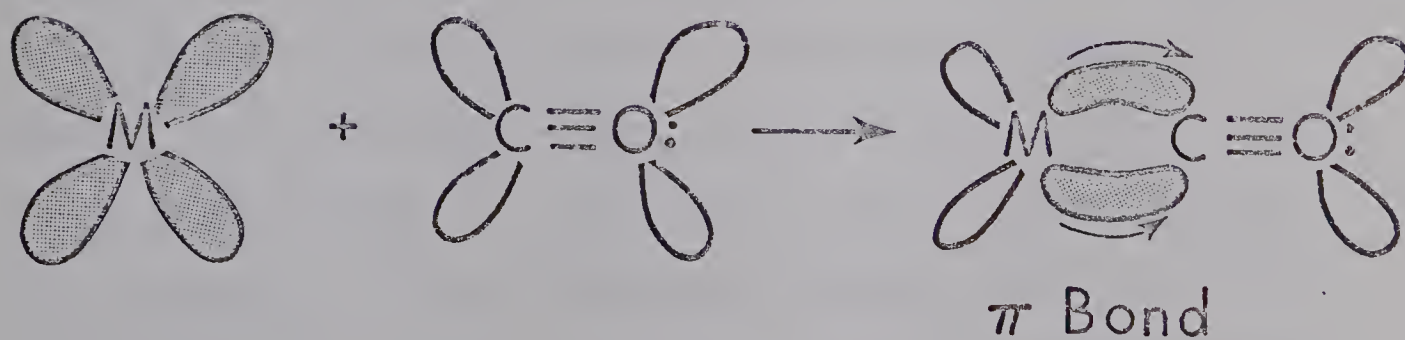
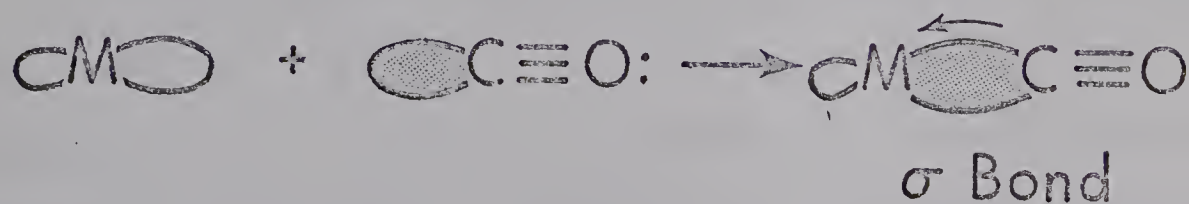
If the bond were considered on the basis of donation of the lone pair only, it would be expected to be extremely weak, since donor ability (Lewis basicity) of carbon monoxide is considered to be quite low. The metal-carbon bond is believed to involve a σ bond resulting from lone pair donation to a vacant metal orbital and a π bond due to back donation of electrons from the filled non-bonding d

orbitals on the metal to the π^* antibonding orbitals of CO. As can be seen in XXXII this will result in the M-CO bond having multiple character. A molecular orbital



XXXII

formulation (XXXIII) shows the situation more clearly and probably more accurately.



XXXIII

The bonding mechanism is said to be synergic since the π bond due to the back donation increases the electron density on carbon, which then strengthens its σ bond formation. This in turn increases the electron density

on the metal and strengthens its π bond formation. It is this overall effect that gives the metal carbonyl its stability.

b. The Carbon-Oxygen Bond

Absorption of infrared radiation by a vibrating molecule is dependent upon a net change of dipole moment of the molecule during a vibration. The frequency at which the absorption occurs will, of course, correspond to the frequency of that particular molecular vibration.

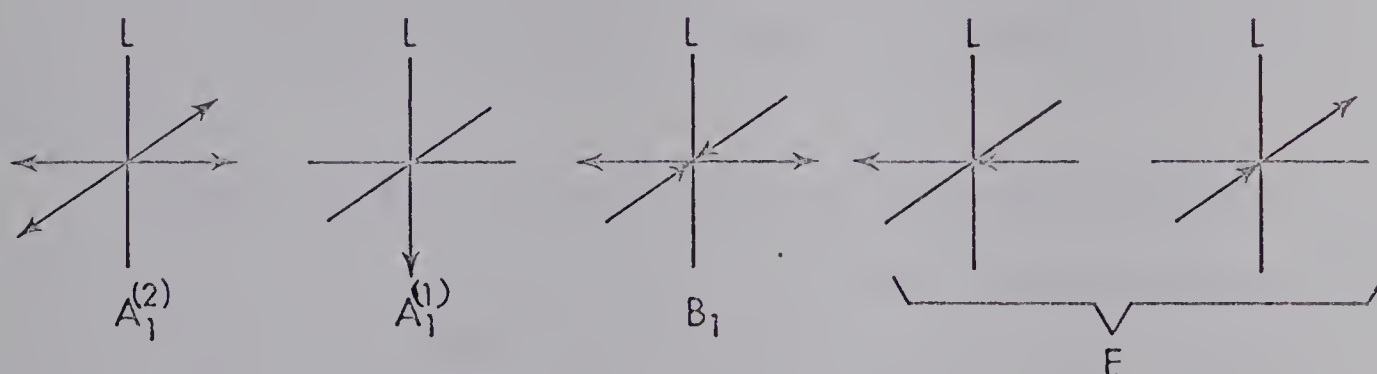
Carbon monoxide exhibits its fundamental vibration frequency at 2143 cm^{-1} . Accordingly, barring other influences, if it becomes coordinated to a metal, the bond order will decrease as shown in the resonance structure XXXII and this will be reflected in the lower frequency of carbonyl absorption bands. Terminal CO groups in binary metal carbonyl molecules are found to absorb in the range $2125\text{--}1900\text{ cm}^{-1}$. Replacing some of the CO groups with ligands of lower π -acceptor ability will cause the remaining CO groups to accept $d\pi$ electrons from the metal to a greater extent to prevent accumulation of negative charge on the metal atom; as a consequence, CO frequencies of substituted metal carbonyls such as $(\text{Ph}_3\text{P})_2\text{Cr}(\text{CO})_4$ tend to be lower.

The vibration of a CO group cannot be considered individually, since it interacts with the vibrations of other parts of the molecule according to the overall symmetry. It is a unique and attractive feature of the vibrations of metal carbonyls that, to a very good approximation, only interactions among the CO groups need be considered. This is the so-called "energy-factoring" approach (120), and is possible because the vibrational frequencies of terminal carbonyl groups are so well separated from other vibrational frequencies.

The discussion of molecular vibrations is facilitated by the use of group theory, which, for example, predicted that a highly symmetrical molecule such as $\text{Cr}(\text{CO})_6$ should have a single infrared-active carbonyl stretching band. More bands are not observed in this case because the other vibrational modes, in view of the symmetry, do not change the dipole moment of the molecule. However, substituting another ligand for a CO group lowers the overall molecular symmetry and increases to three the number of possible infrared active bands.

Molecules of the type $\text{LM}(\text{CO})_5$ (where M is octahedrally coordinated) possess strict C_{4v} symmetry if L is a single atom such as halogen or hydrogen. Idealized C_{4v} symmetry can be applied if L (eg. Ph_3Sn) has a 3- or 4-fold axis,

which would reduce the strict symmetry to Cs. The five CO groups give rise to five fundamental stretching vibrations falling into the symmetry classes A_1 (radial or equatorial), A_1 (axial), B_1 (radial or equatorial) and E (radial, doubly degenerate). These symmetry coordinates are shown in the following diagram (XXXIV). The notation used is that of



XXXIV

Cotton and Kraihanzel (120), where $A_1^{(1)}$ refers to the unique CO group trans to the substituent ligand and $A_1^{(2)}$ represents the symmetrical breathing mode of the other four. Only the two A_1 modes and the E mode are infrared active. Theoretically, spectra of $LMn(CO)_5$ species should show three bands.

The first attempt at assigning the stretching frequencies in molecules of C_{4v} symmetry was made by Orgel (121) in 1962. Orgel used spectra of $CF_3Mn(CO)_5$, $CH_3Mn(CO)_5$ and other related species in assigning the high frequency band (the weakest) to the $A_1^{(2)}$ mode, the more intense of

the lower frequency bands to the E mode since it is doubly degenerate, and the $A_1^{(1)}$ mode to the remaining band of medium intensity. Orgel also pointed out that if it were not for coupling between the two A_1 modes, the one due to the symmetrical breathing of the four axial CO groups would be almost infrared forbidden. The $A_1^{(2)}$ mode would also gain intensity if the equatorial CO groups were not coplanar, or by an electronic migration along the four-fold axis.

Studies of the infrared spectra of $M(CO)_5X$ species ($M = Mn, Re, Tc$; $X = \text{halogen}$) by Hileman and coworkers (122) essentially confirmed Orgel's assignments. Later studies by Wilford and Stone (123) and by Kaesz et al. (73) showed that assignment of the E mode to the most intense band was doubtlessly correct.

c. Use of Force Constant Calculations

The force constant value (k) is representative of the strength of a chemical bond and is related to the vibrational frequency by the equation for the harmonic oscillator:

$$\nu (\text{cm}^{-1}) = \frac{1}{c} \sqrt{\frac{k}{4\pi^2 \mu}}$$

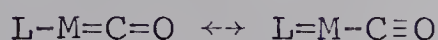
where c is the velocity of light and μ is the reduced mass of the oscillator in grams.

In metal carbonyl chemistry the stretching frequencies of terminal CO groups have been used to calculate the related force constants which provide a clearer insight into the nature of the bonding in these compounds. A rigorous quantitative calculation is complicated. Realizing this fact, Cotton and Kraihanzel(120,124) devised a simplified semiquantitative approach to the calculation of force constants for molecules of the type $ML_x(CO)_{6-x}$ where M is octahedrally coordinated. In this method certain assumptions were made in order to simplify calculations.

Five force constants (two primary, k_1 and k_2 , and three interaction) will be required in a C_{4v} molecule, $LM(CO)_5$. Cotton and Kraihanzel (CK), by assuming a relation between the interaction force constants, were able to reduce the number of independent constants to three, which could be evaluated from a knowledge of the three observed infrared active bands.

In calculating a set of CK force constants, the quadratic equation would produce two sets of values one of which would be imaginary roots. Depending on the assignment of the bands, two sets of real values can be obtained. The "acceptable" set would be one which gives $k_1 < k_2$ and k_i (interaction) as a positive value. That $k_1 < k_2$ can be easily understood since in a substituted molecule $LM(CO)_5$, the CO group trans to the ligand is

competing for the same electron density. Thus, since CO is the best π -acceptor ligand (with the possible exception of PF_3), any other L will cause the trans CO group to acquire a larger fraction of the electron density, increasing the M-C π bond and consequently lowering the bond order of the carbonyl. The π -bonding relationship of L with the M-CO can be shown simply by the following valence bond diagram (XXXV). Lowered order is reflected in a lower value of k_1 . The values of k_2 will not be



XXXV

affected by changes in L to such an extent since there is π -interconnection with the radial CO groups via only one common set of metal d-orbitals. It can be expected that, qualitatively, inductive effects will become more important in this case which will be discussed later in more detail.

RESULTS AND DISCUSSION

a. Spectra of Compounds with C_{4v} Symmetry

1. General Features

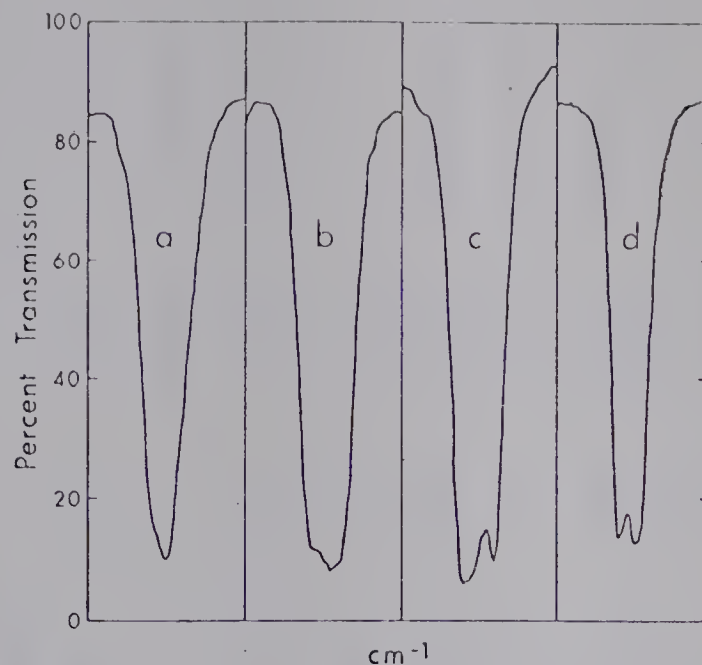
Representative spectra of compounds containing one $\text{M}(\text{CO})_5$ group are shown in Figures 6 through 21 at the end of this chapter.

The general features of infrared spectra obtained for the mono(metal carbonyl) compounds are typical of molecules possessing approximate C_{4v} symmetry. In most cases there are three bands of medium to strong intensity which can be assigned to the $A_1^{(2)}$, $A_1^{(1)}$ and E modes as shown for $(C_6H_5)_3SnRe(CO)_5$ in Figure 6. Assignments were made on the basis of rules set forth by Orgel (121). Molecules of strict C_{4v} symmetry should have only three bands and it is to be expected that additional bands will appear as symmetry is reduced. The extent to which symmetry must be reduced is open to question. In most spectra of the mono-M(CO)₅ compounds investigated in this work, an additional band of weak intensity was observed between the higher energy $A_1^{(2)}$ and the lower energy $A_1^{(1)}$ and E modes. This can be assigned to the B_1 mode which is inactive in strict C_{4v} symmetry. When the threefold symmetry of the R_3Sn ligand is removed as in a compound such as $R_2XSnMn(CO)_5$, the approximation of the molecule to C_{4v} symmetry is presumably worse. An interesting question, therefore, is how unsymmetrical the ligand must be before the molecule displays the five CO stretching bands expected for C_s molecular symmetry.

The last column in Table IX shows that compounds in which the tin atom bears three identical ligands give spectra where the B_1 mode is either weak or non-existent.

This is particularly true of the trihalogenotin series for which the B_1 position was, at best, approximate. Cylindrical symmetry is approached most closely by the X_3Sn and $(CH_3)_3Sn$ derivatives of $Mn(CO)_5$. In less symmetrical cases, the B_1 mode becomes more apparent. Particular examples of note are the $(C_6H_5)_2ClSn$ and $(CH_3)_2(C_6H_5)Sn$ derivatives of $Mn(CO)_5$ in which relative intensities of 2.0 and 2.1 respectively were observed.

The second result of reduced symmetry, splitting of the E mode, as was noted by Wilford and Stone (123), was not definitively observed for most of the compounds investigated in the present work. However, for a number of compounds a problem involving ambiguous assignments for the E and $A_1^{(1)}$ bands did arise. The basis for the problem was two-fold: there was no clear separation of the $A_1^{(1)}$ band from the E and the two bands obtained were of almost equal intensity. This was observed for compounds such as $(C_6F_5)_3SnMn(CO)_5$ (Figure 13) and the sulfur-tin heterocycles. In drawing XXXVI(c) below, intensity considerations suggest the lower frequency band should be assigned $A_1^{(1)}$. While the lower band of XXXVI(d) is slightly more intense and broader, the choice is not clear; both assignments resulting in acceptable force constant values (i.e. $k_1 < k_2$; k_1 positive). The very small intensity difference in this case and in those of the sulfur-tin heterocycles raises



Detail of E and $A_1^{(1)}$ bands in certain compounds (cyclohexane solution). A 45-cm^{-1} segment of each spectrum is shown: (a) $\text{C}_6\text{H}_5(\text{C}_6\text{F}_5)_2\text{SnMn}(\text{CO})_5$; (b) $(\text{C}_6\text{H}_5)_2\text{C}_6\text{F}_5\text{SnMn}(\text{CO})_5$; (c) $\text{C}_6\text{H}_5\text{Cl}_2\text{SnMn}(\text{CO})_5$; (d) $(\text{C}_6\text{F}_5)_3\text{SnMn}(\text{CO})_5$.

XXXVI

the possibility that the doublet may result from a splitting of the doubly degenerate E mode as was observed by Wilford and Stone for fluoroorganic derivatives of $\text{Mn}(\text{CO})_5$ and $\text{Re}(\text{CO})_5$ (123). If the splitting is genuine and due to the removal of the degeneracy, the origin would be the bulky groups on tin. A more definite conclusion about the splitting would have been possible if a less intense band (the $A_1^{(1)}$) had been observed in any of these cases. Only one compound, $(\text{C}_6\text{H}_5)\text{Cl}_2\text{SnRe}(\text{CO})_5$ (Figure 7) showed a separate, clearly recognizable $A_1^{(1)}$ band, which made it possible to attribute the incipient splitting to the E mode.

TABLE IX

CARBONYL STRETCHING FREQUENCIES, ASSIGNMENTS AND APPROXIMATE

FORCE CONSTANTS FOR $R_3SnM(CO)_5$ MOLECULES^a

Compound	Frequencies, cm^{-1} b		Force Constants m dynes/A			cm^{-1}	
	$A_1^{(2)}$	E	$A_1^{(1)}$	k_1	k_2	k_i	B_1
							(found)
$(C_6H_5)_3Sn$	2093(4.8)	2002 (10)	2002 (10)	16.34	16.64	0.226	2027 (1.5)
$(CH_3)_3Sn$	2089(m)	1991 (s)	1998 (m)	16.29	16.49	0.240	----- ^c
$(CH_3)_2ClSn$	2101(m)	2006 (s)	2015 (m)	16.57	16.72	0.234	2039 (w)
$(C_6H_5)_2ClSn$	2103(4.8)	2108 (10)	2018 (10)	16.59	16.87	0.212	2044 (2.0)
$(C_6H_5)Cl_2Sn$	2114(5.6) 2114	2031 (10) 2023	2023(9.6) 2031	16.65 16.82	17.07 16.97	0.208 0.223	2056 2050
Cl_3Sn	2126 (m)	2046 (s)	2039 (m)	16.91	17.31	0.204	----- ^c
Br_3Sn	2122 (m)	2043 (s)	2037 (m)	16.88	17.26	0.201	2060 ^c
$(C_6H_5)_2I_1Sn$	2102(5.2)	2014 (10) ^d	2014 (10)	16.52	16.82	0.219	2041 (1.6)
$(C_6H_5)I_2Sn$	2110(5.0) 2110.	2027 (10) 2020	2020 (8.0) 2027	16.75 16.61	16.92 17.01	0.223 0.210	2047 2052
I_3Sn	2117(3.6)	2037 (10)	2031 (4.8)	16.78	17.16	0.203	2058 (0.5) ^c

L =

1 135 1

TABLE IX (continued)

Compound	Frequencies, cm^{-1} b		Force Constants m dynes/Å				cm^{-1}	
	$A_1^{(2)}$	E	$A_1^{(1)}$	k_1	k_2	k_i	B_1 (calcd)	B_1 (found)
L =								
$\text{LMn}(\text{CO})_5$								
$(\text{C}_6\text{H}_5)_2(\text{C}_6\text{F}_5)\text{Sn}$	2101(5.8) 2101	2012 (10) 2016	2016 (9.9) 2012	16.57 16.48	16.79 16.84	0.221 0.213	2039 2042	2038 (1.8)
$(\text{C}_6\text{H}_5)(\text{C}_6\text{F}_5)_2\text{Sn}$	2108(3.9)	2020 (10)	2020 (10)	16.62	16.92	0.220	2047	2047 (1.0)
$(\text{C}_6\text{F}_5)_3\text{Sn}$	2116(5.4) 2116	2029 (10) 2034	2034 (9.9) 2029	16.86 16.75	17.06 17.12	0.217 0.207	2055 2059	2059 (1.4) 2059
$(\text{C}_6\text{H}_5)_3\text{Sn}$	2107(4.3)	2025 (10)	2017 (7.5)	16.55	16.97	0.207	2050	----- ^d
$(\text{CH}_3)_3\text{Sn}$	2104(4.0)	2019 (10)	2019 (10)	16.60	16.89	0.212	2045	2044 ^c (0.5)
$(\text{CH}_3)_2(\text{C}_6\text{H}_5\text{S})\text{Sn}$	2095(4.4)	2000 (10)	2007 (8.7)	16.43	16.62	0.230	2029	2029 (2.1)
$(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{S})\text{Sn}$	2098(3.5)	2010 (10)	2010 (10)	16.46	16.75	0.220	2037	2033 (1.1)
$(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_5\text{S})\text{Sn}$	2098(5.5)	2010 (10)	2010 (10)	16.46	16.75	0.220	2037	2035 (1.2)
$(\text{C}_6\text{H}_5)(\text{CH}_3\text{S})_2\text{Sn}$	2102(4.4)	2013 (10)	2013 (10)	16.51	16.81	0.222	2040	2041 ^c (0.7)
$(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{S})_2\text{Sn}$	2103(4.8)	2017 (10)	2011 (8.5)	16.46	16.86	0.216	2043	2045 (0.7)
$(\text{CH}_3)_2(\text{C}_6\text{F}_5\text{S})\text{Sn}$	2099(4.1)	2003 (10)	2012 (8.2)	16.52	16.67	0.236	2032	2035 (1.9)
$(\text{C}_6\text{H}_5)_2(\text{C}_6\text{F}_5\text{S})\text{Sn}$	2102(5.3) 2102	2014 (10) 2009	2009 (9.7) 2014	16.44 16.54	16.82 16.76	0.230 0.221	2041 2037	2042 (1.1)

TABLE IX (continued)

Compound	Frequencies, cm^{-1} b		Force Constants m dynes/A			cm^{-1}	
	$A_1^{(2)}$	E	$A_1^{(1)}$	k_1	k_2	k_i	B_1 B_1
L =							(found) (calcd)
$(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_5\text{S})_2\text{Sn}$	2111(5.7) 2111	2028 (10) 2024	2024 (9.3) 2028	16.75 16.67	16.98 17.03	0.217 0.209	2050 2053
$(\text{C}_6\text{F}_5\text{S})_3\text{Sn}$	2117(6.3)	2037 (10)	2032 ^e (8.8)	16.80	17.16	0.203	2061
$\text{S}(\text{CH}_2)_2\text{SSn}(\text{C}_6\text{H}_5)$	2106(5.0) 2106	2022 (10) 2013	2013 (10) 2022	16.49 16.68	16.93 16.82	0.212 0.229	2048 2041
$\text{S}(\text{CH}_2)_2\text{SSnCl}$	2114(4.8) 2114	2031 (10) 2026	2026 (9.8) 2031	16.81 16.71	17.01 17.08	0.219 0.210	2053 2056
$\text{SCHCH}_2\text{SSn}(\text{C}_6\text{H}_5)$ CH_3	2102(4.5) 2102	2012 (10) 2016	2016 (9.9) 2012	16.57 16.48	16.79 16.84	0.223 0.216	2039 2042
$\text{S}(\text{CH}_2)_3\text{SSn}(\text{C}_6\text{H}_5)$	2101(5.1)	2012 (10)	2012 (10)	16.49	16.79	0.222	2039
$[(\text{C}_6\text{H}_5)_2\text{Sn}(\text{SCH}_2-)]_2$	2097(5.1)	2008 (10)	2008 (10)	16.43	16.72	0.221	2035
$\text{SC}(\text{CN})=\text{C}(\text{CN})\text{SSn}(\text{C}_6\text{H}_5)^f$	2115(6.3)	2028 (10) ^g	2028 (10)	-----	-----	-----	-----
LRe(CO) ₅							
L = $(\text{C}_6\text{H}_5)_3\text{Sn}$	2114(3.6)	2012 (3.6)	2003 (8.1)	16.36	16.86	0.257	2043
$(\text{CH}_3)_3\text{Sn}$	2108(2.6)	2003 (10)	2003 (10)	16.38	16.72	0.261	2035
							2042 (1.1) 2014 (1.4)

TABLE IX (continued)

Compound	Frequencies, cm^{-1} b		Force Constants			cm^{-1}	
	$A_1^{(2)}$	E	$A_1^{(1)}$	k_1	k_2	k_i	B_1 (calcd) B_1 (found)
LRe(CO)_5							
$(\text{C}_6\text{H}_5)_2\text{ClSn}$	2125(2.3)	2022 (10)	2010 (8.8)	16.48	17.01	0.266	2052 2058 (1.8)
$(\text{C}_6\text{H}_5)\text{Cl}_2\text{Sn}$	2135(1.9)	2037(9.8) ^e	2022	16.65	17.26	0.251	2067 2071 (0.9)
Cl_3Sn	2141(1.7)	2044 (10)	2030 (5.5)	16.78	17.37	0.249	2074 2077 ^c
Br_3Sn	2143(3.8)	2046 (10)	2030 (8.0)	16.78	17.40	0.250	2076 2070 ^c
$(\text{C}_6\text{H}_5)\text{I}_2\text{Sn}$	2131(1.7)	2033 (10)	2020 (7.0)	16.62	17.19	0.250	2063 2067 (0.6)
I_3Sn	2137(2.3)	2042 (10)	2026 (7.7)	16.71	17.33	0.244	2071 2057 (0.5)
$(\text{C}_6\text{H}_5\text{S})_3\text{Sn}$	2130(3.1)	2033 (10)	2015 (8.6)	16.54	17.18	0.251	2062 ^d
$(\text{CH}_3\text{S})_3\text{Sn}$	2127(3.7)	2027 (10)	2014 (8.5)	16.53	17.10	0.255	2059 2046 ^c (0.8)

a. Here, actual formulae are used for the sake of clarity.

b. Relative intensity given in parentheses refers to the relative band height on a linear transmittance scale, with the most intense band taken as 10. In some cases, data obtained from earlier work and values were not available. Two sets of values indicate ambiguities (see text).

c. Indistinct; position uncertain. d. Not observed. e. Shoulder. f. Chloroform solution. g. Broad and unresolved.

One other feature of the spectra which warrants discussion is the degree of separation of the two A_1 modes. For $Mn(CO)_5$ compounds separations were approximately 90 cm^{-1} while the $Re(CO)_5$ series showed higher values of 105 to 115 cm^{-1} . These values are not as high as those observed by El-Sayed and Kaesz (125) for the pentacarbonyl halides nor for the afore-mentioned compounds of Wilford and Stone (123). The higher values for $Re(CO)_5$ species can be attributed to a greater degree of coupling between the two modes and the effect is reflected in higher interaction force constants. For example, k_i for $Br_3SnMn(CO)_5$ is $0.201\text{ m.dynes/\AA}^{\circ}$ whereas for the rhenium analog a value of $0.250\text{ m.dynes/\AA}^{\circ}$ is calculated.

2. Application of Force Constant Calculations

In molecules $LMn(CO)_5$, the ligand L and the CO group trans to it can both undergo π bonding with the same two transition metal d orbitals. The π acceptor strength of L will be reflected directly by the force constant, k_1 . The greater the L-M π sharing becomes, the higher the force constant.

In this present work, force constants were obtained by the Cotton-Kraihanzel (CK) approximation. The values obtained for k_1 , k_2 and k_i are shown in Table IX. It was of interest to observe the effect of various groups on tin on the relative values of the k_1 , k_2 and k_i .

Considering k_1 values first it is seen that $\text{Mn}(\text{CO})_5$ derivatives range from 16.29 m dynes/ \AA when L is $(\text{CH}_3)_3\text{Sn}$ to 16.91 m dynes/ \AA for $\text{Cl}_3\text{SnMn}(\text{CO})_5$. For $\text{Re}(\text{CO})_5$ species, values are slightly higher at the lower end (16.36 m dynes/ \AA for $(\text{C}_6\text{H}_5)_3\text{Sn}$) but slightly lower for the trihalides (16.78 m dynes/ \AA for Cl_3Sn and Br_3Sn). The value of 16.91 m dynes/ \AA found for $\text{Cl}_3\text{SnMn}(\text{CO})_5$ is to date the highest value known for carbonyl compounds of Mn and Re. Only one higher value, for cis-(F_3P) $_3\text{Mo}(\text{CO})_3$, of 16.98 has been found (126) for compounds to which the CK treatment has been applied.

On the basis of π effects only, the high k_1 values for trihalogenotin derivatives suggest that tin in these instances possesses high π acceptor ability; this ability being a result of the high electronegativity of chlorine, causing contraction of d-orbitals on tin. A similar conclusion about Cl_3Sn bonded to platinum (II) has been reached by Parshall (127) using ^{19}F nmr measurements. In this case, vacant 5d orbitals of tin were considered to overlap with filled platinum 5d orbitals in the π -acceptor component of the tin-platinum bond. Infrared studies by Ugo et al. (128) on X_3Sn ($\text{X} = \text{C}_6\text{H}_5, \text{Cl}$) derivatives of $\text{Mn}(\text{CO})_5$ and $\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ compounds reported during the course of the present work produced the same conclusions concerning Sn-Mn π (d-d) overlap.

These conclusions were drawn on the basis of stretching frequencies only.



The usefulness of k_1 values in interpreting the π -acceptor abilities of ligands is well-recognized but most likely provides an incomplete picture. Recently, Graham (129) reported a study which took into account the inductive effects operating through the metal-ligand σ bond. The quasi-theoretical (or semi-empirical) approach distinguished between π -withdrawal and σ -withdrawal effects by ligands in a number of substituted metal carbonyls, some of which were prepared in this present work.

Using both k_1 and k_2 values, Graham found that ligands which contained tin or other Group IV metals all acted as π acceptors to some degree. However $\text{Cl}_3\text{SnMn}(\text{CO})_5$ by this method was not as strong a π -acceptor as might be considered using only k_1 values. It did exhibit some degree of σ -withdrawal ability which might be expected on the basis of electronegativity considerations alone. All of the tin compounds where organic groups were involved were found to be σ donors.

3. Electronegativity Estimations

As Graham points out (129), the inductive effect of a ligand should act equally on all five CO groups through the three d_{π} orbitals. This effect is observed in the

stretching frequencies of a series of $\text{Mn}(\text{CO})_5$ compound starting with $\text{L} = (\text{C}_6\text{H}_5)_3\text{Sn}$. Replacement of phenyl groups by halogen atoms one at a time brings about a steady increase in $\nu(\text{CO})$ for all bands; this effect being due to the increased electronegativity of the ligand. Using the frequency of the $\text{A}_1^{(2)}$ band, it is seen that values increase in increments of 7-12 cm^{-1} for any given halogen. Figure 4 shows that there is a

Ligand	$\nu(\text{A}_1)^{(2)} \text{ cm}^{-1}$	$\Delta\nu \text{ cm}^{-1}$	Ligand	$\nu(\text{A}_1)^{(2)} \text{ cm}^{-1}$	$\Delta\nu \text{ cm}^{-1}$
Ph_3Sn	2093		Br_3Sn	2122	
Ph_2ClSn	2103		Ph_2ISn	2102	
PhCl_2Sn	2114		PhI_2Sn	2110	
Cl_3Sn	2126		I_3Sn	2117	

linear relationship between the sum of the Pauling electronegativities (Cl : 3.16, Br : 2.96, I : 2.66) (130) of halogens on tin and the value of the stretching frequency of the $\text{A}_1^{(2)}$ band. An analogous relationship has been found by Patmore and Graham (43) for compounds of the type $\text{R}_n\text{X}_{3-n}\text{GeCo}(\text{CO})_4$ ($\text{R} = \text{C}_6\text{H}_5, \text{CH}_3$; $\text{X} = \text{halogen}$) and by Kasenally and coworkers (131) for some Group IB metal derivatives of $\text{Mn}(\text{CO})_5$.

A similar incremental change in $\nu(\text{CO})$ for the $\text{C}_6\text{F}_5\text{-Sn}$ derivatives prepared in this present work suggested that

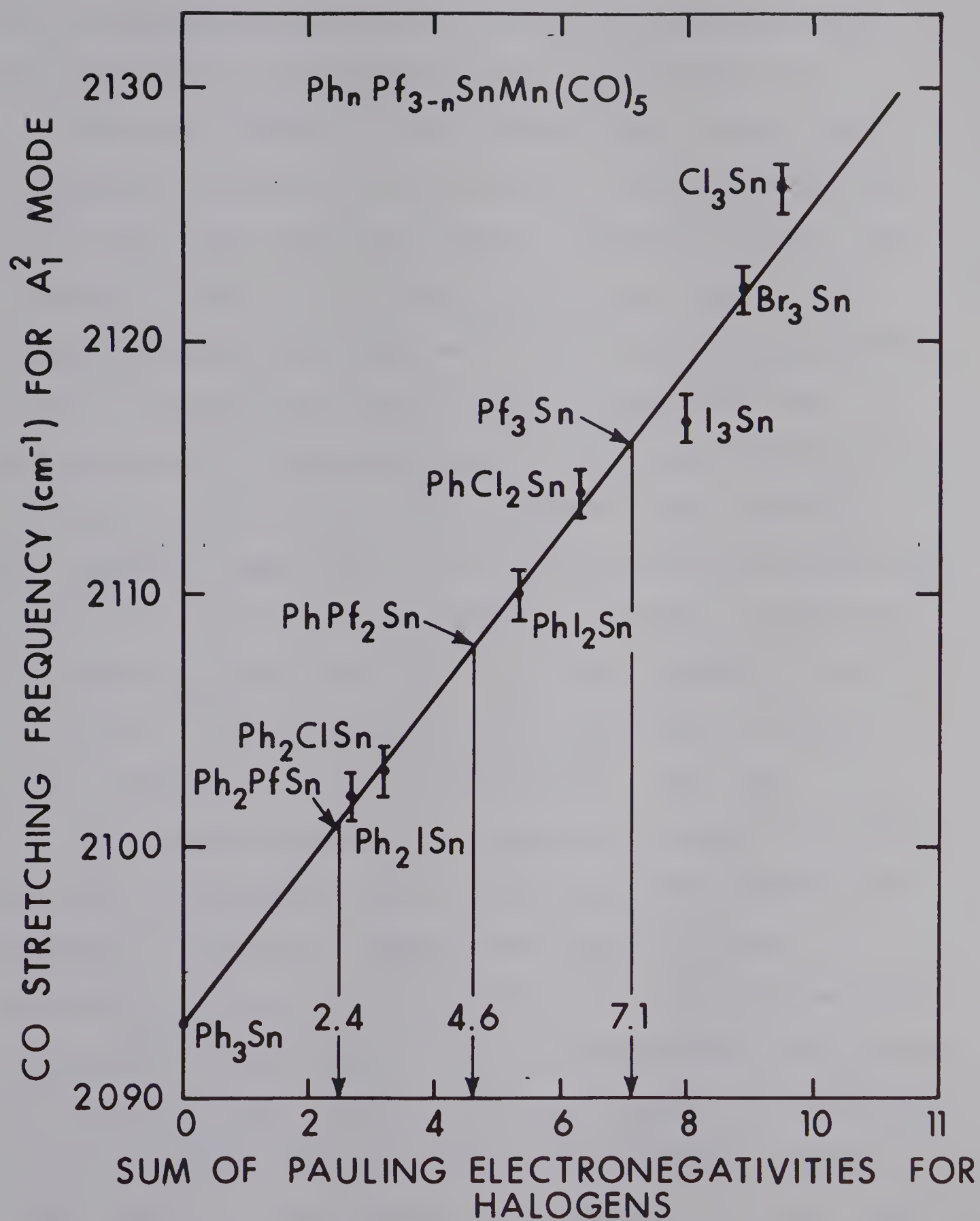


FIGURE 4

an electronegativity estimate for the C_6F_5 group could be obtained by interpolation from the straight line plot shown in Figure 4. The average value is 2.4 which is slightly lower than iodine (2.66). Previous estimates placed the value somewhat higher, a Mössbauer study (132) yielding a value of 2.68 while proton nmr results on C_6F_5 -Sn derivatives suggested a value intermediate between those of chlorine and bromine (93). Naturally, the effective electronegativity of the C_6F_5 group depends on the way it can interact with the rest of the molecule. For example, application of the frequency-electronegativity relation to the series $C_6F_5Mn(CO)_5$, $ClMn(CO)_5$, $BrMn(CO)_5$ and $IMn(CO)_5$ would place the C_6F_5 group between Br and I (the $A_1^{(2)}$ frequencies of these compounds are 2130, 2138, 2133 and 2125 cm^{-1} respectively. (122, 123)

An identical qualitative approach was used to obtain an electronegativity value for the C_6F_5S derivatives reported in Chapter V. Results are shown in Figure 5, an average value of 2.7 being obtained. This higher value, compared with the C_6F_5 group is to be expected since sulfur is electronegative (2.58) in its own right. It is possible that the values $\nu(CO)$ are lower than might be expected since sulfur is also capable of π bonding with tin. Back-donation of filled d orbitals of sulfur into the vacant d orbitals of tin would tend to lower the carbonyl stretching frequency.

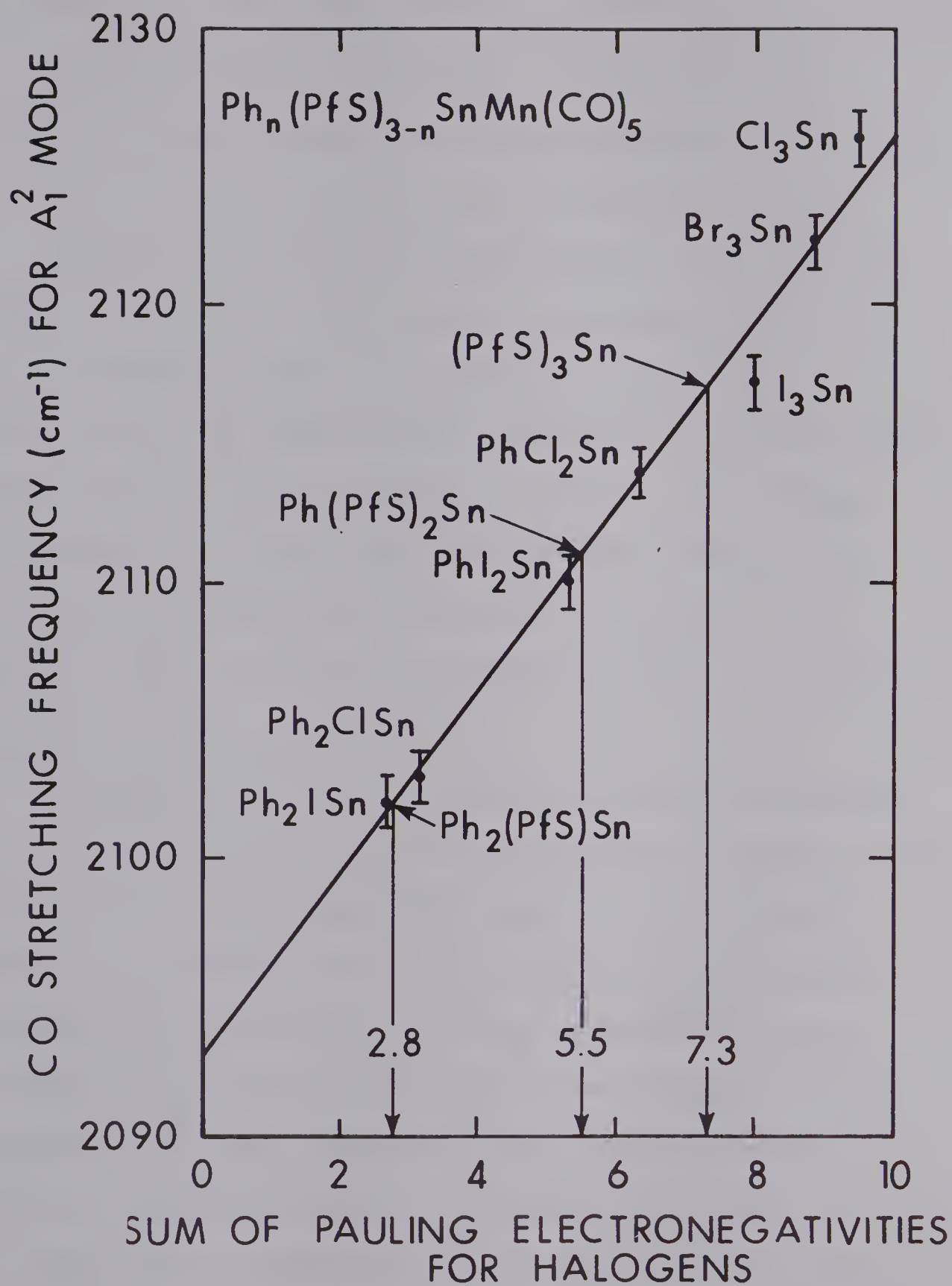


FIGURE 5

b. Spectra of the Bis- and Tris-Metalcarbonyl Derivatives

Typical spectra of the bis- and tris-manganese and rhenium carbonyl species are shown in Figures 22 through 30. Band frequencies are given in Tables X and XI.

Compounds of the type $R_2Sn[M(CO)_5]_2$ (R = halogen, alky, aryl; M = Mn, Re) can occur in two conformations, one of which is shown in drawing VII in Chapter II. In either case, C_{2v} symmetry is expected. One conformation would give 8 infrared bands; the other, the maximum of 10 bands. No more than 8 bands were observed for any of the derivatives prepared in this work. The smaller number could be attributed to weak or accidentally degenerate bands, however.

Although there was no attempt at band assignments it is of interest to note that the general pattern of the spectra of the bis compounds resembles that found by Patmore and Graham (43) for analogous cobalt carbonyl compounds $R_2Sn[Co(CO)_4]_2$. A pair of bands at higher frequency is observed, separated from a group at lower frequency. If only the upper pair are considered, an obvious change of relative intensity of the upper to the lower band is noted as the substituents on tin become larger. The highest energy band in $Cl_2Sn[Mn(CO)_5]_2$ is very weak with an intensity of 0.4 relative to the most intense band of the spectrum. In $(C_6F_5)_2Sn[Mn(CO)_5]_2$,

TABLE X

CARBONYL STRETCHING FREQUENCIES OF BIS(MANGANESE OR RHENIUM) TIN COMPOUNDS

Compound	cm^{-1}									
$\text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$	2099(1.4)	2074(5.3)	2091(1.1)	2004 (10)	2002 ^a (9.2)	1984(4.8)	1961 ^b (0.6)	---		
$\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$	2100(3.4)	2078(8.9)	2029(4.9)	2009 (10)	2006 ^a (8.9)	2002(8.7)	1986 (9.0)	1961 ^b (1.0)		
$\text{Cl}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$	2119(0.4)	2093(5.9)	2056(2.0)	2030 (10)	2024 (4.0)	2011(1.3)	2002 (3.9)	---		
$\text{Pf}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$	2113(2.4)	2090(8.1)	2043(3.4)	2026((10)	2024 (9.9)	2020(8.8)	2008 (2.4)	2000 (7.8)		
$(\text{MeS})_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$	2107(1.9)	2083(6.9)	2036(1.9)	2017 (10)	2009 (6.2)	1992(6.9)	1978 (0.9) ^b	1963 (0.9) ^b		
$(\text{PhS})_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$	2108(1.8)	2088(5.7)	2044(2.1)	2020 (10)	2012 (4.7)	1991(6.1)	---	---		
$\overline{\text{S}(\text{CH}_2)_2\text{SSn}[\text{Mn}(\text{CO})_5]_2}$	2108(0.6)	2081(5.7)	2037(1.7)	2018 (10)	2013 ^a (4.9)	1993(4.5)	---	---		
$\text{Me}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$	2114(1.4)	2092(6.5)	2070(1.1)	2044 (0.5)	2010 (2.9)	2009 (10)	1998 (9.0)	1987 (9.6)		
$\text{Ph}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$	2118(0.9)	2099(5.1)	2039(2.1)	2016 ^a (9.7)	2015 (10)	2001(5.4)	1995 ^b (2.8)	1987 (8.9)		
$\text{Cl}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$	2125(0.3)	2116(5.4)	2065(2.5)	2034 (10)	2020 (6.1)	2015(3.8)	2002 (7.3)	---		
$(\text{MeS})_2\text{Sn}[\text{Re}(\text{CO})_5]_2$	2124(0.9)	2106(5.3)	2047(1.7)	2022 (10)	2007 (5.5)	1994(8.6)	---	---		
$\overline{\text{S}(\text{CH}_2)_2\text{SSn}[\text{Re}(\text{CO})_5]_2}$	2125(0.8)	2103(5.6)	2048(2.1)	2024 ^a (9.7)	2022 (10)	2010(4.1)	1994 (8.1)	1963 ^b (0.6)		
$\overline{\text{SCHCH}_2\text{SSn}[\text{Re}(\text{CO})_5]_2}$ Me	2124(1.2)	2103(5.0)	2048(1.9)	2022 (10)	2008 (3.5)	1991(7.6)	---	---		

a. Shoulder

b. Assigned as ^{13}C Satellites

an intensity of 2.4 is measured for the same band. In the cobalt series (43), it was suggested that this intensity difference could be explained in terms of varying bond angles. A similar explanation might be applicable in this work.

The tris derivatives can be considered to possess formal C_{3v} symmetry. For any conformation of the $M(CO)_5$ groups the maximum number of predicted infrared bands is 8 and again in some cases the observed number falls short of this value.

Here, too, assignments cannot be made readily due to the complex nature of the system. However, the general pattern of the spectra again has two bands at higher frequency separated by a large group at lower frequency. It is interesting to note in this case that the two upper bands do not shift appreciably with changes in the substituent on tin and in the halogen derivatives of $Sn[Mn(CO)_5]_3$, all three have exactly the same frequency values of 2093 and 2080 cm^{-1} for these two bands.

An interesting aspect common to both bis- and tris derivatives is that one cannot apply "local symmetry" rules. That is, each $M(CO)_5$ unit cannot be treated independently, in which case only five bands would be observed. A greater number of bands suggests coupling between the metal carbonyl groups via d orbitals on tin is occurring. This has been suggested previously by Patmore and Graham (43)

TABLE XI

CARBONYL STRETCHING FREQUENCIES OF TRIS(MANGANESE OR RHENIUM) TIN COMPOUNDS

Compound	cm ⁻¹									
MeSn[Mn(CO) ₅] ₃	2105(0.4)	2072(3.8)	2074 (9.5)	2005 (6.4)	1994(10)	1985(3.3)	1973 ^a (0.5)	1963 ^a (0.6)	---	
nBuSn[Mn(CO) ₅] ₃	2103(1.2)	2083(1.6)	2070 (9.5)	2037 (1.1)	2017(6.6)	2012(9.8)	2003 (9.0)	1992 (10)	1984 (5.6)	
ViSn[Mn(CO) ₅] ₃	2107(0.4)	2084(0.9)	2073 (9.3)	2017 (9.9)	2006(5.6)	1996(10)	1987 (5.9)	1974 ^a (0.8)	1962 ^a (0.6)	
PhSn[Mn(CO) ₅] ₃	2106(0.6)	2085(6.4)	2039 ^b (2.0)	2023 ^b (5.5)	2015(10)	2005(6.8)	1995 (8.3)	1987 (5.6)	---	
ClSn[Mn(CO) ₅] ₃	2093(0.4)	2080(8.3)	2037 (5.8)	2030 ^b (3.0)	2020(8.0)	2005(10)	1989 (4.2)	---	---	
BrSn[Mn(CO) ₅] ₃	2093(1.2)	2080(8.7)	2050 (1.2)	2036 (4.9)	2030(3.2)	2020(8.2)	2003 (10)	1988 (3.9)	---	
ISn[Mn(CO) ₅] ₃	2093(1.4)	2080(7.8)	2044 (4.7)	2037 (5.9)	2029(5.3)	2020(8.6)	2005 (10)	1989 (5.1)	---	
MeSSn[Mn(CO) ₅] ₃ ^c	2107(0.8)	2077(6.4)	2073 (6.7)	2032 (3.4)	2026(4.5)	2017(10)	2004 (7.3)	2000 (8.0) 1987 (6.0)	1997 (7.8) 1964 (2.1)	
MeSn[Re(CO) ₅] ₃	2118(0.3)	2090(7.9)	2044 (1.3)	2017 (10)	2007(8.2)	1999(4.6)	1993 (9.5)	1988 (9.5)	1954 ^a (1.0)	
n-BuSn[Re(CO) ₅] ₃	2119(0.4)	2090(8.1)	2026 ^b (2.7)	2016 (10)	2007(7.9)	1999(5.2)	1992 (9.3)	1988 (9.7)	---	
ViSn[Re(CO) ₅] ₃	2119(0.2)	2092(8.0)	2044 (0.8)	2030 (2.4)	2020(10)	2008(8.1)	1995 (8.3)	1988 (9.8)	1953 ^a (0.8)	
PhSn[Re(CO) ₅] ₃	2121(0.5)	2093(8.0)	2044 (1.5)	2032 (3.5)	2020(10)	2008(7.6)	2000 ^b (5.3)	1996 (7.7)	1988 (10)	
ClSn[Re(CO) ₅] ₃	2117(0.4)	2101(5.9)	2044 (4.5)	2034 (2.7)	2026(10)	2013(4.9)	2006 (7.7)	1992 (9.3)	---	

a. Assigned as ¹³C Satellite.

b. Shoulder.

c. Slow decomposition in solution gave rise to additional bonds.

for analogous $\text{Co}(\text{CO})_4$ derivatives. An interesting anomaly was found in a series of anionic species of the type $(\text{CO})_5\text{M}-\text{M}'\text{X}_2-\text{M}(\text{CO})_5^{2-}$ ($\text{M} = \text{Cr}, \text{W}, \text{Mo}$; $\text{M}' = \text{Sn}, \text{Ge}$; $\text{X} = \text{Br}, \text{I}$) (45). Only half or less of the expected bands were observed suggesting that no coupling occurred between the two $\text{M}(\text{CO})_5$ groups.

c. Spectra of Ditin Species

The spectra of the ditin species (Figures 31, 32, and 33) show that coupling of vibrations on individual $\text{M}(\text{CO})_5$ groups on the metal atoms must be taken into account. The infrared spectrum of the MnSnSnMn compound in Figure 31 shows at least seven medium or strong bands and shoulders indicating that coupling across two intervening tin atoms is occurring.

An interesting trend is noted if the compound with a direct Sn-Sn linkage is compared with those (Figures 32 and 33) which have single bridging sulfur groups between the tin atoms. In the Mn-Sn-S-Sn-Mn compound, the lower frequency region is what would be expected of a somewhat asymmetric C_{4v} system. However, in the high frequency area, the single $\text{A}_1^{(2)}$ band has been replaced by a doublet.

If, now, the lone sulfur atom is replaced by the $-\text{S}(\text{CH}_2)_2\text{S}-$ group (Figure 33) a normal three band spectrum attributable to an isolated $\text{Mn}(\text{CO})_5$ group is obtained.

It was in fact possible in this case to calculate the force constant values. The calculated B_1 position of 2035 cm^{-1} was in good agreement with the observed value of 2034 cm^{-1} showing that a C_{4v} assignment was valid. It could be concluded from these observations that the degree of coupling between the $\text{Mn}(\text{CO})_5$ groups decreases as expected as the two tin atoms become more remote to each other. Of course, in the compound containing the aliphatic carbon chain, no coupling would be expected since there are no d orbitals available through which this could occur.

In attributing the extra bands to electronic coupling in the Sn-Sn and Sn-S-Sn system, it must be pointed out that additional bands can also arise because of conformational isomers or to a steric interaction of equatorial carbonyl groups on the manganese atoms. With respect to the former alternative, it is known that a conformational effect on metal carbonyl bands does exist (133,134).

Because of insolubility of the solids in cyclohexane, spectra of the two compounds with twin bridging sulfur atoms were not obtained with the usual high resolution obtained in this solvent. A spectrum of the tetrakis- $\text{Mn}(\text{CO})_5$ compound obtained in dichloromethane showed 6 bands (Figure 37) and resembled spectra of the bis- $\text{Mn}(\text{CO})_5$

derivatives as it had 2 high frequency absorptions separated by four at lower frequency. In this case the question arises as to whether the two $\text{Sn}[\text{Mn}(\text{CO})_5]_2$ units can be considered as isolated, as is suggested by the spectrum or whether it is necessary to consider the molecule as a whole. The molecule would possess formal D_{2h} symmetry which predicts a maximum of 8 or 9 bands depending on the conformation of the $\text{Mn}(\text{CO})_5$ groups. It would be difficult to conclude whether coupling of vibrations through the sulfur atoms was occurring in this case.

The compound $[(\text{CO})_5\text{MnSn}(\text{C}_6\text{H}_5)\text{S}]_2$ presented the possibility of cis and trans isomers (Chapter V; drawings XXVIII and XXIX). The point group of the cis isomer would be C_{2v} and would, on this basis show a maximum of 8 or 9 bands depending on the conformation of the metal carbonyl groups. The more symmetrical (C_{2h} point group) trans isomer would have 5 infrared-active vibrations and 5 bands were observed. This is not conclusive evidence that the trans isomer was the one obtained as the exclusive product but does suggest that this is the more likely choice. Here again, though, the possibility of applying local symmetry cannot be ruled out.

d. Spectra of the Phosphine Derivatives

1. $[(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{Mn}_2(\text{CO})_9$ and $[(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{Mn}_2(\text{CO})_8$

The triphenylphosphine nonacarbonyl has been discussed

by Ziegler, Haas and Sheline (117) and by Wawersik and Basolo (116) in terms of C_{4v} symmetry assuming axial substitution by the phosphine. Using this assumption, 5 infrared active bands ($2E, 3A_1$) are predicted and this number is reported by both sources.

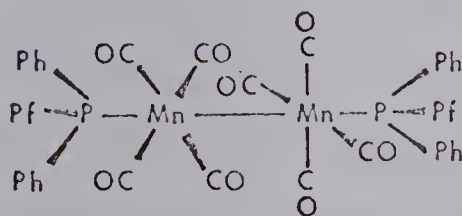
It might be expected that the presence of the C_6F_5 group on phosphorus will reduce the symmetry somewhat and that the number of infrared bands would increase. In fact, 7 bands were found in a spectrum which had a pattern (Figure 35) similar to that reported by Ziegler and coworkers (117). There is a slight increase in frequency in comparable bands as shown below. The

<u>$L = (C_6H_5)_3P$</u>		<u>$L = (C_6F_5)(C_6H_5)_2P$</u>
<u>(Ref. 117)</u>	<u>(Ref. 116)</u>	<u>(Figure 35)</u>
2093 (m) cm^{-1}	2098 (s) cm^{-1}	2094 (3.5) cm^{-1}
2011 (m)	2015 (s)	2016 (5.0)
1994 (vs)	1997 (ss)	2000 (10)
-----	-----	1987 (1.9)
1973 (m)	1969 (w)	1977 (3.9)
-----	-----	1966 (1.0)
1939 (m)	1937 (s)	1940 (3.3)
in n-hexane	in p-xylene	in cyclohexane

higher frequencies can be attributed to the increased electron withdrawal by the more electronegative C_6F_5

group. The band at 1966 cm^{-1} is of weak intensity and could represent a small amount of the disubstituted compound which has its most intense absorption at the same frequency. The other extra band at 1987 cm^{-1} may be the result of lowered symmetry at the phosphorus site.

The bis-phosphine compound, $[(\text{C}_6\text{F}_5)(\text{C}_6\text{H}_5)_2\text{P}]_2\text{Mn}_2(\text{CO})_8$, has a spectrum of a much simpler nature owing to higher molecular symmetry. One strong band at 1966 cm^{-1} and two weaker bands at 1998 and 2009 cm^{-1} respectively are observed (Figure 34). Recent crystallographic studies (135) on $[(\text{C}_6\text{H}_5)_3\text{PMn}(\text{CO})_4]_2$ have shown a structure in which the two halves of the molecule are turned at 45° to each other (XXXVII). A structure of this type possesses D_{4d} symmetry



XXXVII

which predicts 2 bands designated as E_1 and B_2 , the former being the most intense. The extra band found in the $(\text{C}_6\text{F}_5)\text{P}(\text{C}_6\text{H}_5)_2$ derivative again might be indicative of decreased symmetry. The effect of increased electronegativity of the ligands is seen below in comparison

with the stretching frequencies of the $(C_6H_5)_3P$ species (115,136).

$L = (C_6H_5)_3P$		$L = (C_6F_5)(C_6H_5)_2P$
<u>(Ref. 115)</u>	<u>(Ref. 136)</u>	<u>(Figure 34)</u>
-----	-----	2009 (2.1)
1980 (sh)	1985	1998 (3.8)
1956 (vs)	1957	1966 (10)
(in $CHCl_3$)	(in CCl_4)	(in C_6H_{12})

2. $R_3SnMn(CO)_4[P(C_6H_5)_2C_6F_5]$ Compounds

The stretching frequencies for the compounds $R_3SnMn(CO)_4[P(C_6H_5)_2(C_6F_5)]$ ($R = C_6H_5, Cl$) are given in Table XII. Because of low solubility of the solids in hydrocarbon solvents, it was necessary to use chloroform, which tended to broaden the bands. For the $(C_6H_5)_3Sn$ species, two bands ($A_1^{(2)}$ and E) which would be expected for formal C_{4v} symmetry, are seen. In the trihalide case, an extra band at highest frequency is also observed.

The triphenylphosphine compounds prepared by Gorsich (19) have been studied in the infrared by Ugo et al. (128). The effect of increased electronegativity of the phosphine is again noticeable in a slight shift of frequencies to higher energies. It is also noted that for the $(C_6H_5)_3P$

derivatives the $A_1^{(2)}$ mode was not observed. It would not be expected to be overly intense since, as Orgel (121) pointed out, without coupling to the $A_1^{(1)}$ mode, (which no longer exists) the $A_1^{(2)}$ band should be almost forbidden. The fact that it does appear with greater intensity in this present work might indicate that there is a greater degree of non-coplanarity of the four CO groups in these compounds.

The infrared results of the four phosphine- $Mn(CO)_4Sn$ species mentioned here suggest that the two ligands are trans to each other. A cis configuration would be indicated by a 3 or 4 bands as has been shown by Angelici (137) and Basolo (138) for compounds of the type cis-phosphine $Mn(CO)_4X$ ($X = Cl, Br, I$) and cis- $Mn(CO)_4X_2^-$. The reason why phosphine groups should go trans to tin ligands and cis to halogens is apparent in a consideration of the nature of the Mn-C bond. Graham (129) has concluded that halogens are π donors and σ acceptors. Since they are π donors the multiple bond character of the Mn-C linkage should increase, thus decreasing the lability of the CO group. This has been pointed out also by Angelici and Basolo (138). The phosphine will go cis to a halide in $Mn(CO)_5X$ because the planar CO groups are more labile. Conversely, since organotin groups have been shown to be π acceptors, the lability of the CO group trans to the tin atom will be

TABLE XII

CARBONYL STRETCHING FREQUENCIES OF MISCELLANEOUS MANGANESE CARBONYL DERIVATIVES

Compound	Solvent ^b	cm ⁻¹						
[Ph ₂ SnMn(CO) ₅] ₂	A	2103(2.9)	2098(3.9)	2094 (2.6)	2044(1.0)	2033(1.4)	2016(8.4) 2004(9.8)	2009 (10) 1999 ^a (7.5)
[Ph ₂ SnMn(CO) ₅] ₂ S	A	2098(3.7)	2093(4.8)	2031 (1.5)	2007(10)	2002(9.8)		
[PhSnMn(CO) ₅ S] ₂	A	2100(4.5)	2041(1.9)	2018 (9.8)	2012(10)	1989(2.3)		
{[(CO) ₅ Mn] ₂ SnS}	B	2103(3.2)	2084(8.6)	2038 (3.6)	2017(10)	2008(9.7)	1994(5.8)	
(P ⁱ Ph ₂ P)Mn ₂ (CO) ₉	A	2094(3.5)	2016(5.0)	2000 (10)	1987(1.9)	1977(2.9)	1966(1.0)	1940 (3.3)
(PhPh ₂ P) ₂ Mn ₂ (CO) ₈	A	2009(2.1)	1998(3.8)	1966 (10)				
Ph ₃ SnMn(CO) ₄ (PPh ₂ Pf)	C	1995(1.0)	1955(10)					
Cl ₃ SnMn(CO) ₄ (PPh ₂ Pf)	C	2086(0.4)	2040(1.1)	2000((10)				

a. Shoulder.

b. A = cyclohexane; B = dichloromethane, C = chloroform.

greater. The resulting trans disubstituted compound will be more stable due to the overall π bonding situation. Gorsich (19) has shown that phosphines do indeed substitute CO trans to the tin atom.

EXPERIMENTAL SECTION

Infrared spectra obtained in this work were recorded using a Perkin-Elmer 337 Spectrophotometer. Whenever possible, a cyclohexane solution of the material under investigation was used. This solvent has 80-100% transmittance in the region of 2200-1800 cm^{-1} . It provided excellent spectral band resolution and extremely narrow band widths compared with other common solvents. Cells used were of KBr with a 0.5 mm path length. Through experience it was found that a concentration of about one milligram of material per milliliter of cyclohexane provided spectra where the most intense peak gave 80-90% transmittance. It was often necessary to warm the cyclohexane to get the necessary amount of material into solution. Samples were prepared by dissolving the material in cyclohexane contained in a one dram vial and adding the solution directly to the sample cell.

The carbonyl region was recorded in expanded form on a Texas Instruments Servo-Riter recorder. Each expanded spectrum was calibrated above and/or below the region of

interest by introducing gas cells containing carbon monoxide or deuterium bromide into the sample beam at the appropriate times during a continuous run. Sample bands were then measured by interpolation using CO band no. 31 or DBr band no. 13 as reference points. In some cases the highest energy band appeared too near CO band no. 31 to make measurement from this point possible. Accordingly, band no. 30 was used and the necessary readjustments in wave number calculation made.

It should also be pointed out that spectra as represented in the figures in this chapter were obtained at one of two scanning rates. Part way through the work, a motor which ran the region $4000-1200\text{ cm}^{-1}$ in 16 minutes was replaced by one which covered the same region in 72 minutes (at a rate of 39 cm^{-1} per minute). Older spectra were obtained with the servo-Riter running at 6 inches/minute while more recent ones were obtained at 3 inches/minute ($5.21\text{ cm}^{-1}/\text{cm}$ of chart paper).

Carbonyl stretching frequencies are reported in Tables IX-XII. Unless note is made to the contrary, all spectra were run in cyclohexane with the same solvent as reference. Numbers in parentheses represent relative intensities of the bands calculated on a linear transmittance scale, with the most intense band taken as 10.

It was felt that this method was more representative of the intensities than the older w , m , s notation.

The force constant values for the mono(metal carbonyl) compounds were obtained by the Cotton Kraihanzel approximation (120) using a computer program prepared by Mr. R. S. Gay.

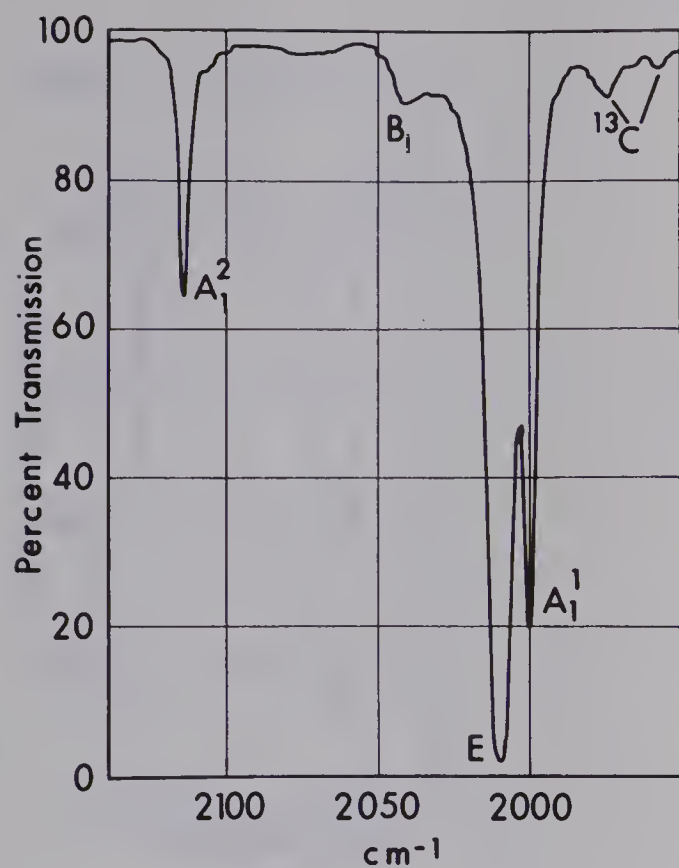


FIGURE 6

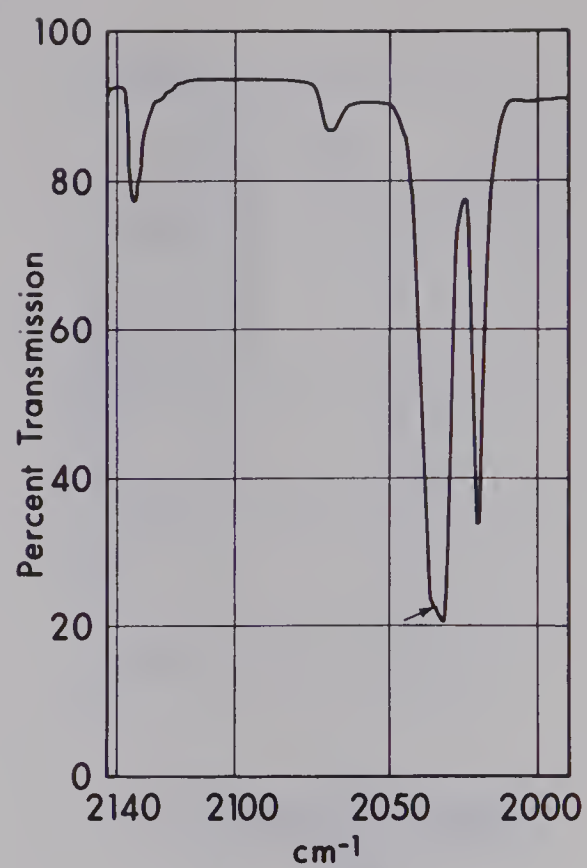


FIGURE 7

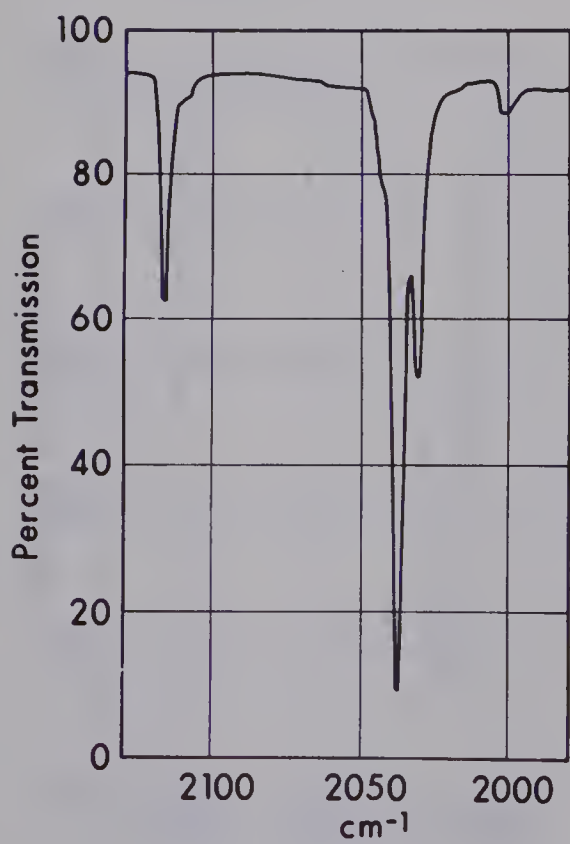


FIGURE 8

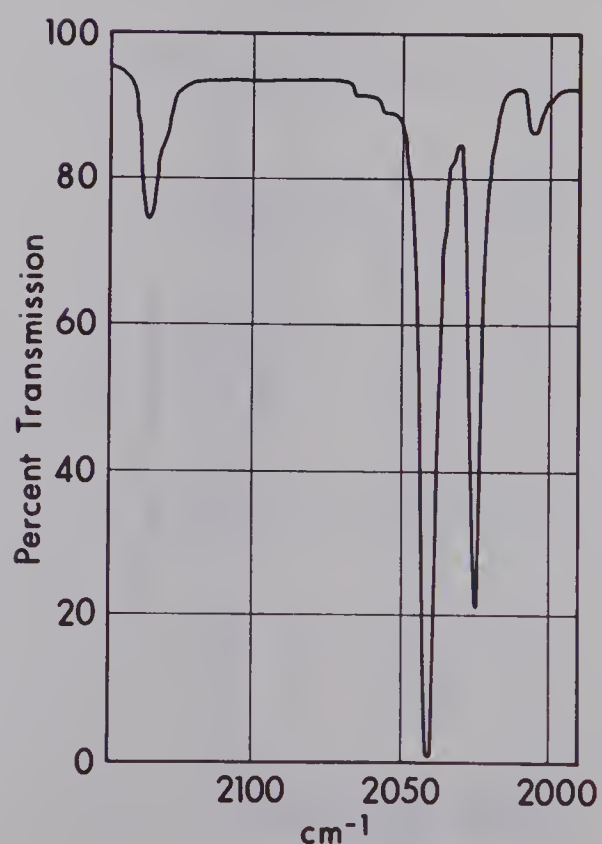


FIGURE 9

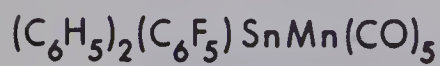
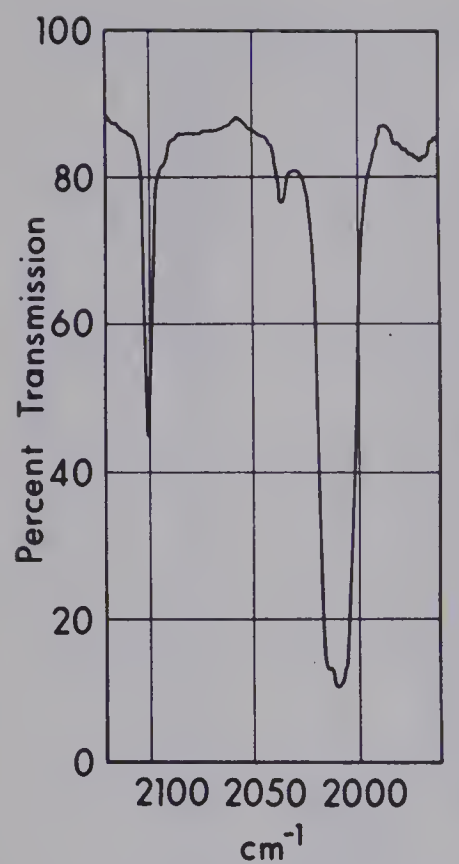


FIGURE 10

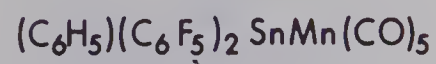
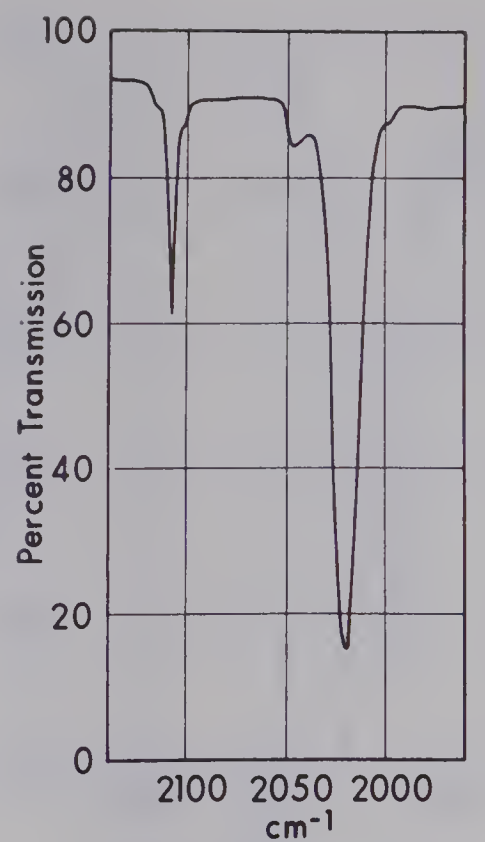


FIGURE 11

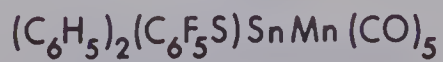
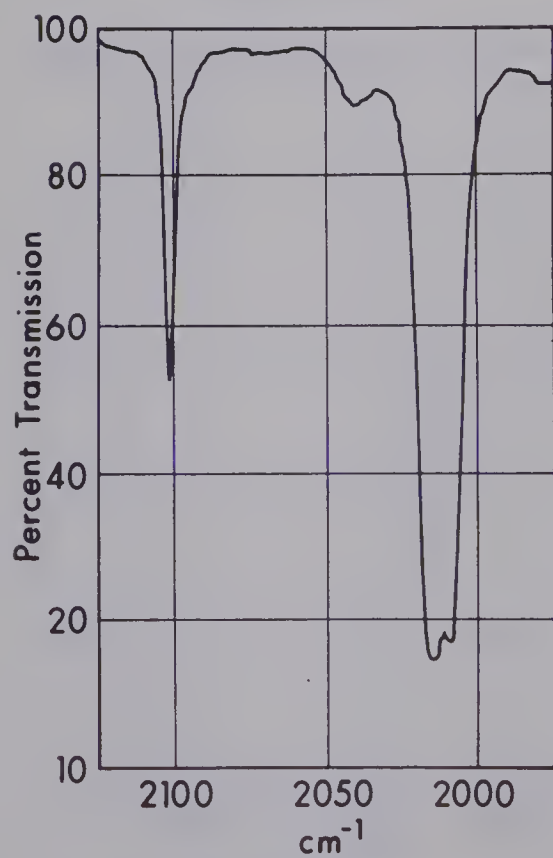


FIGURE 12

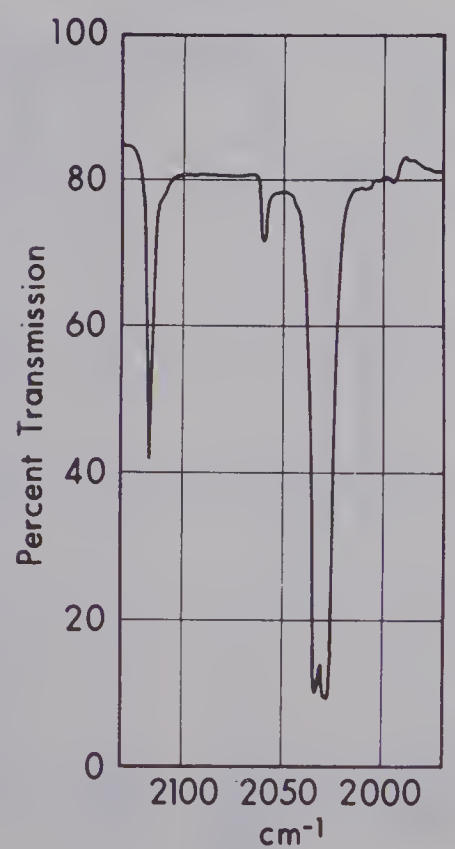


FIGURE 13

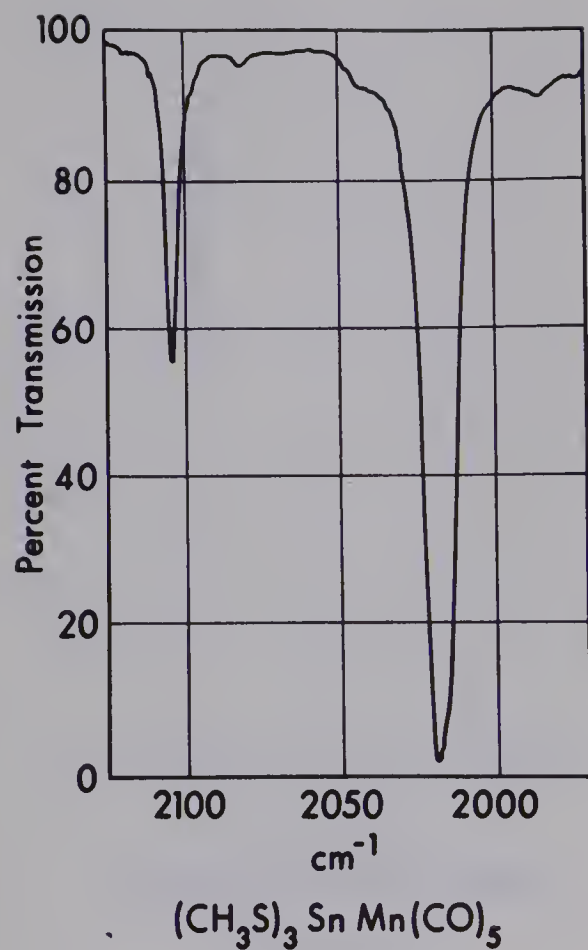


FIGURE 14

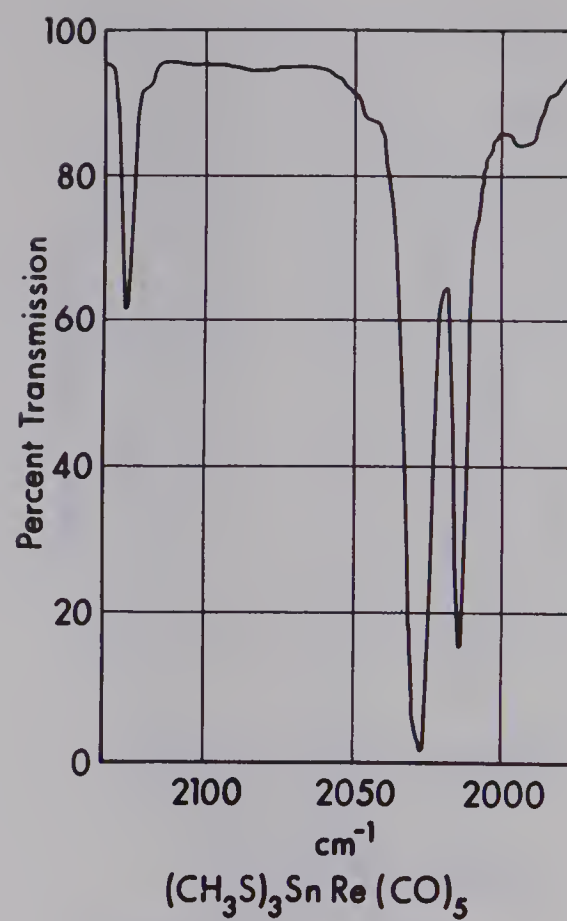


FIGURE 15

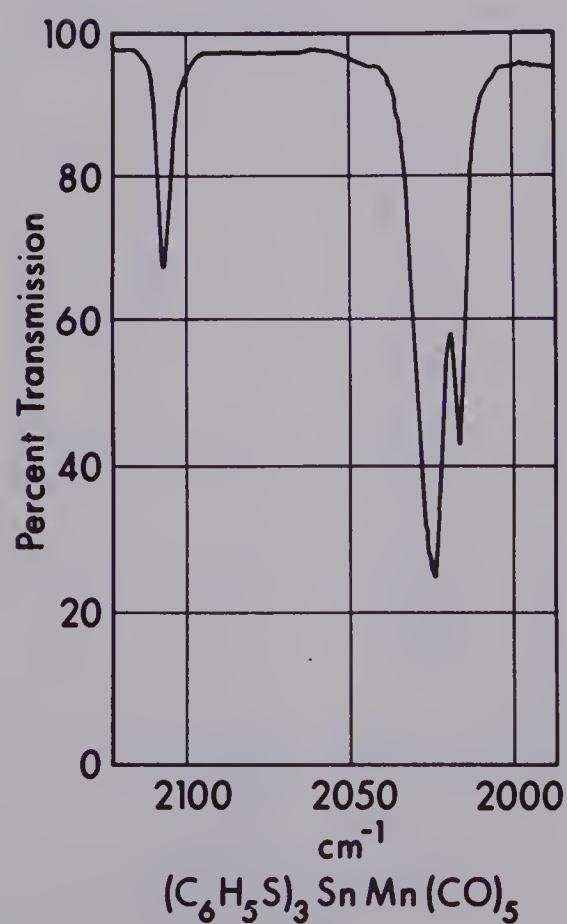


FIGURE 16

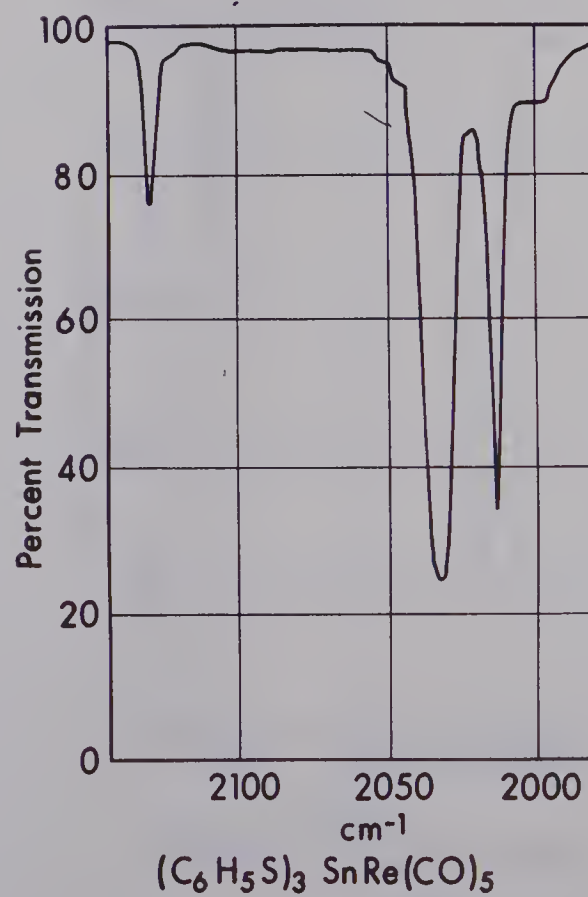


FIGURE 17

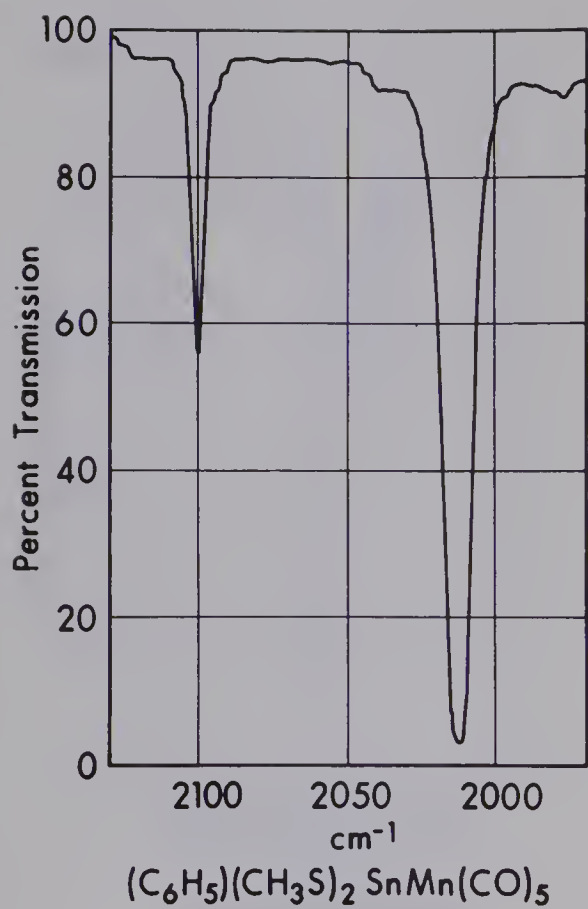


FIGURE 18

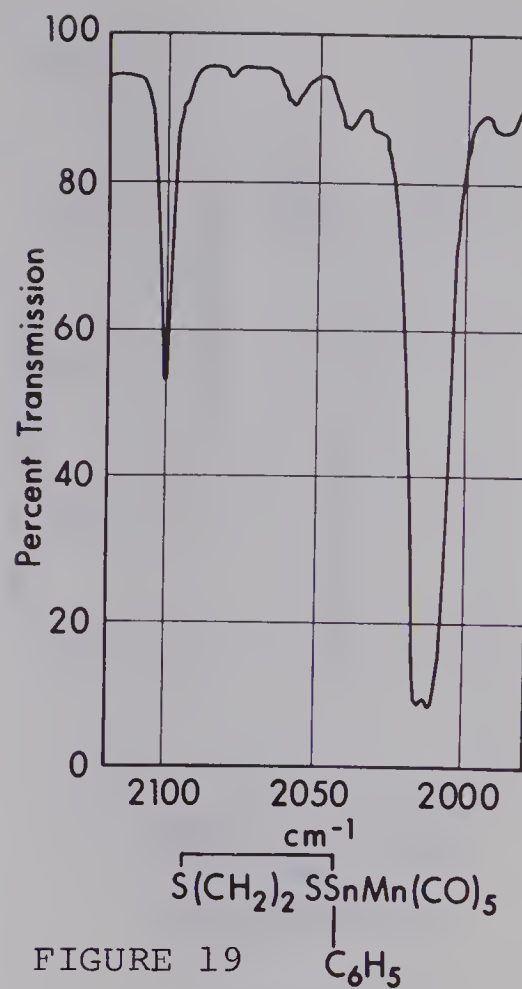


FIGURE 19

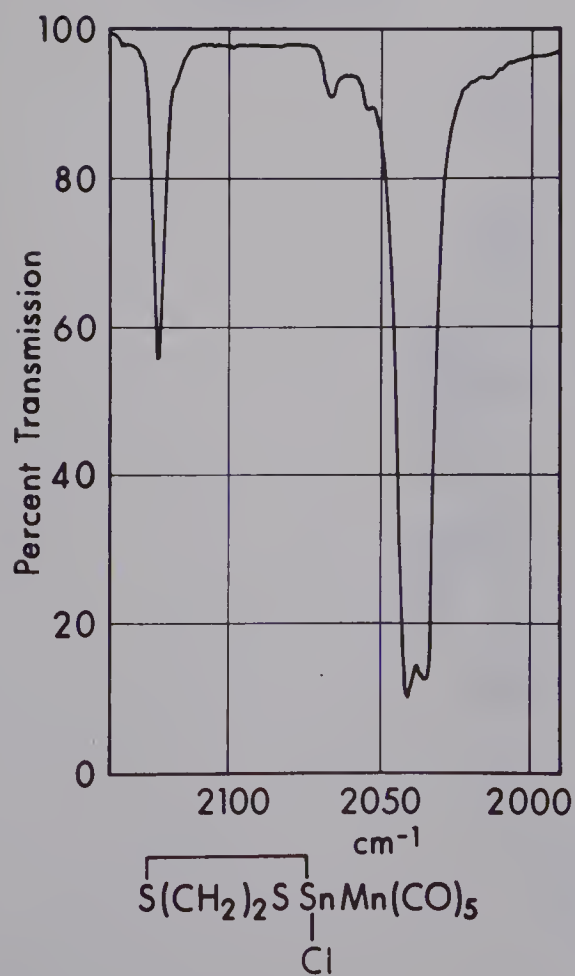


FIGURE 20

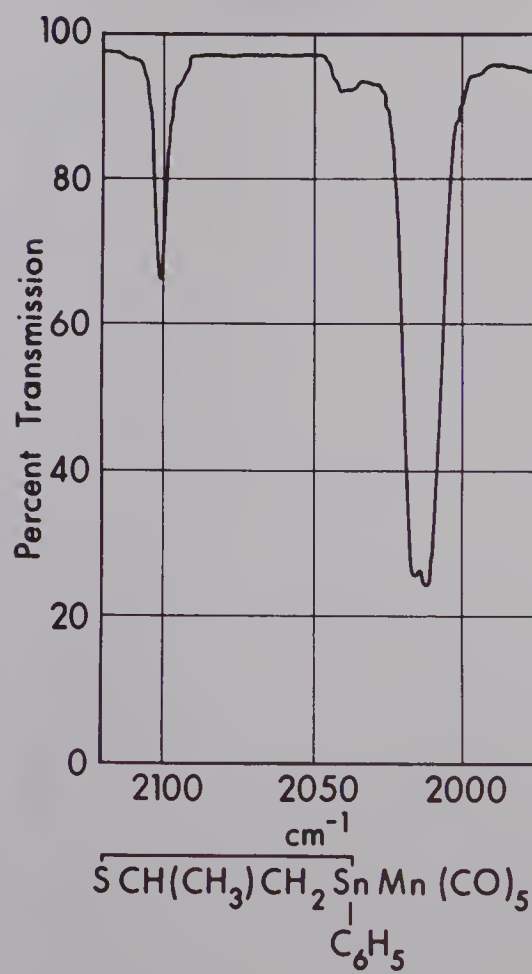


FIGURE 21

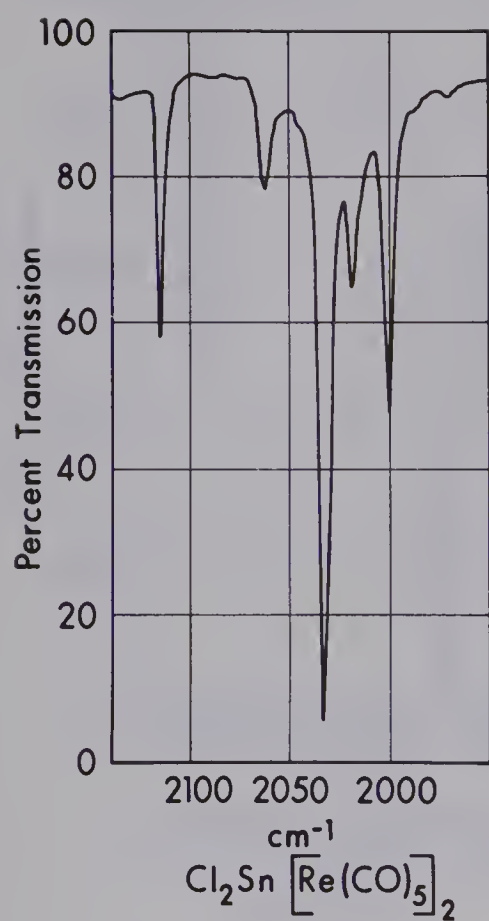


FIGURE 22

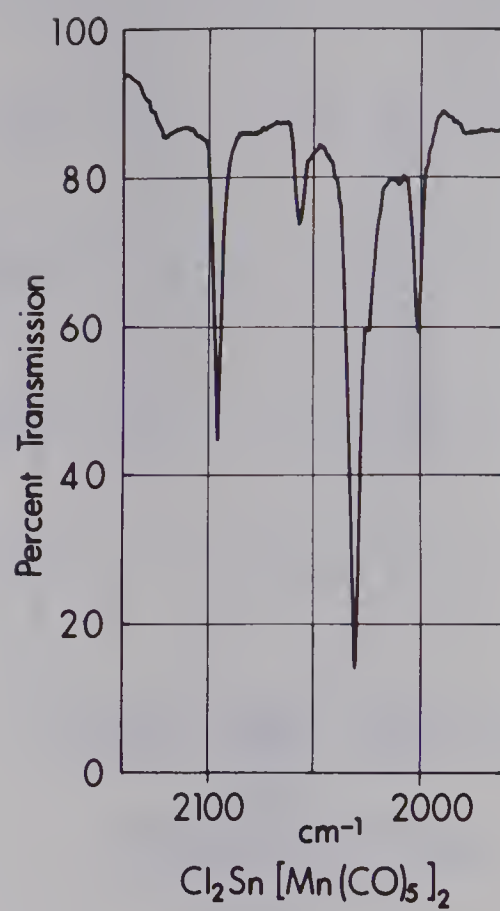


FIGURE 23

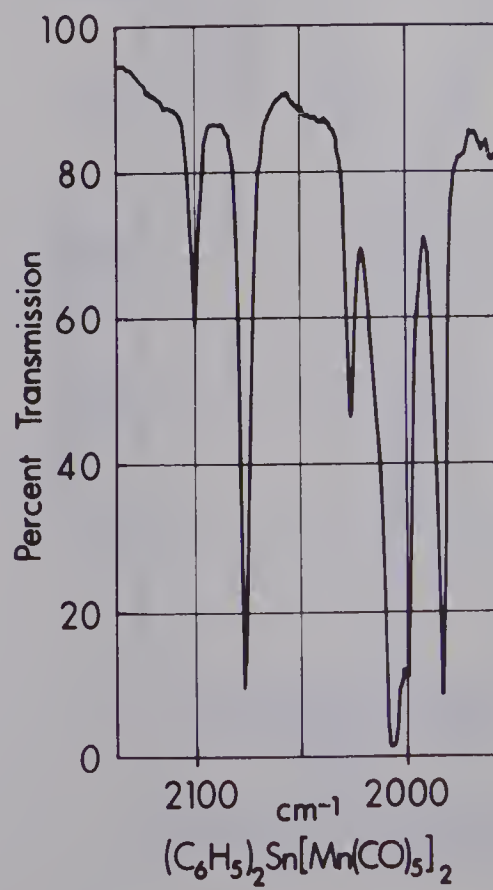


FIGURE 24

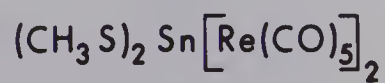
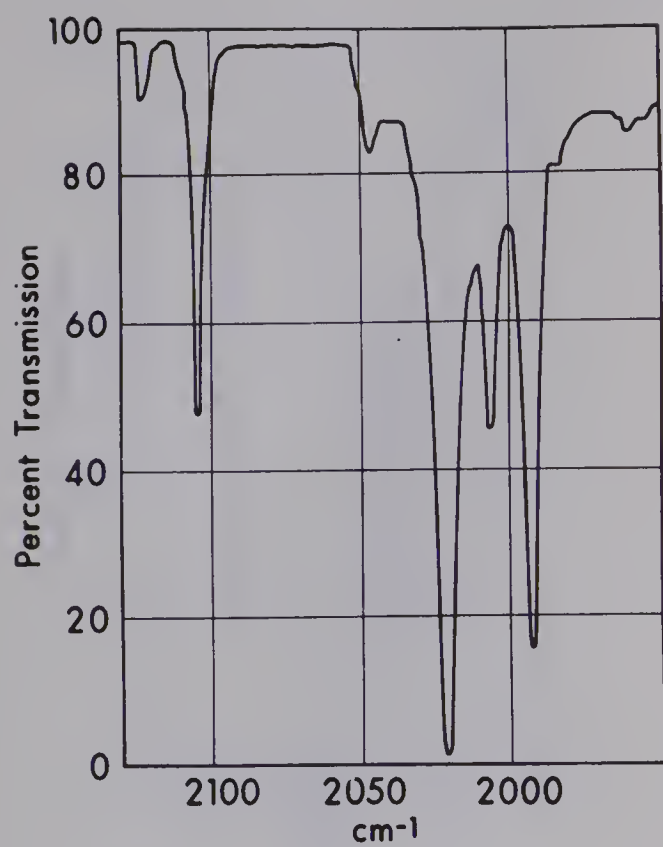


FIGURE 25

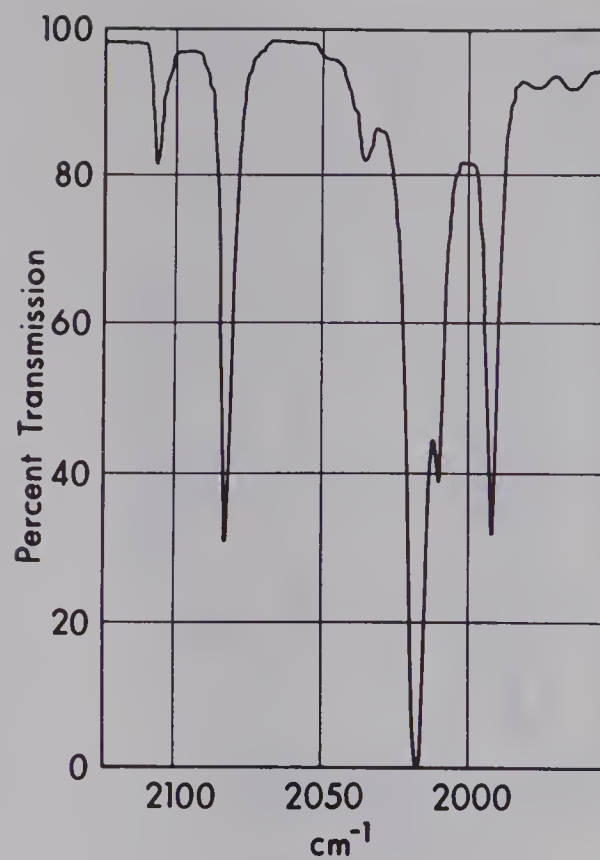


FIGURE 26

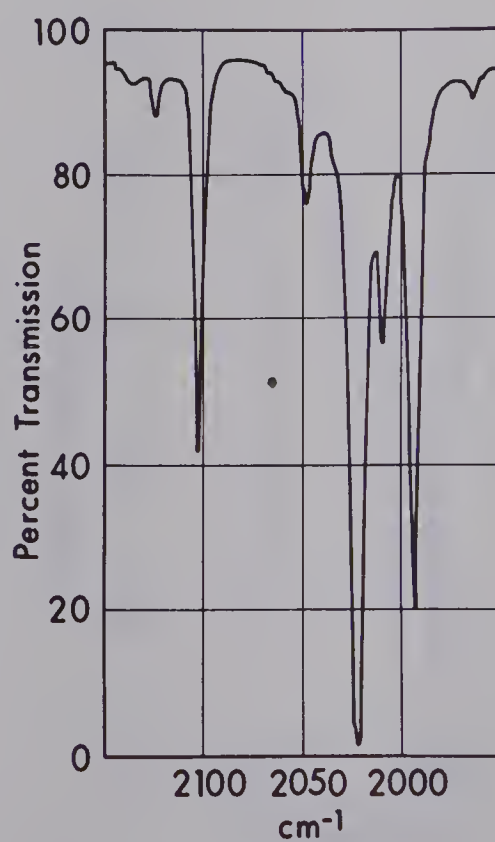


FIGURE 27

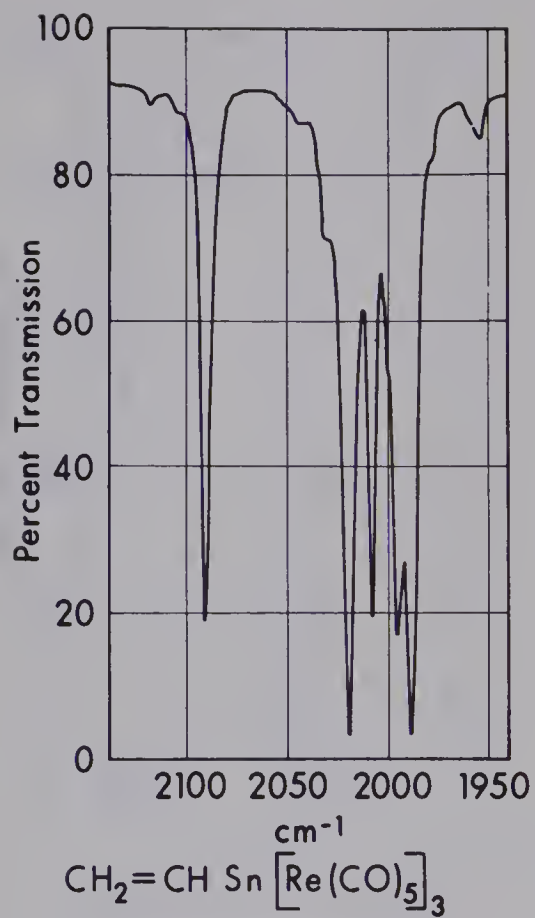


FIGURE 28

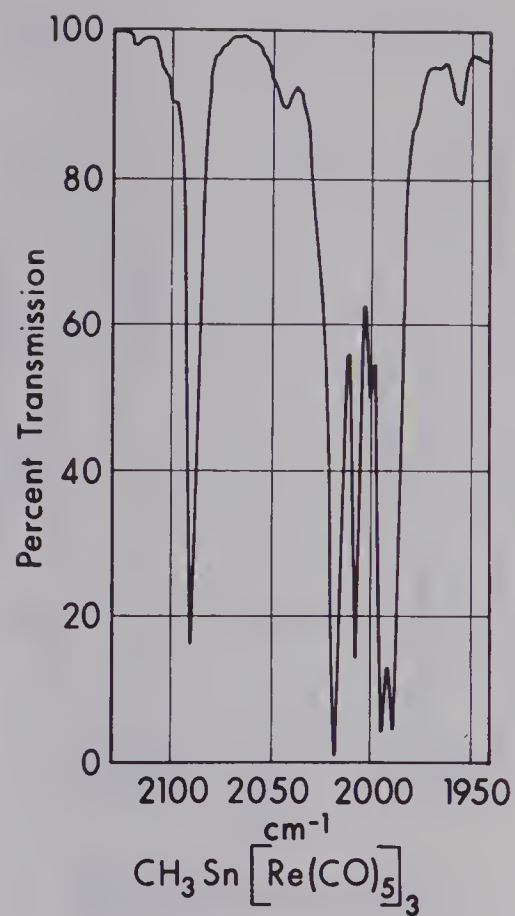


FIGURE 29

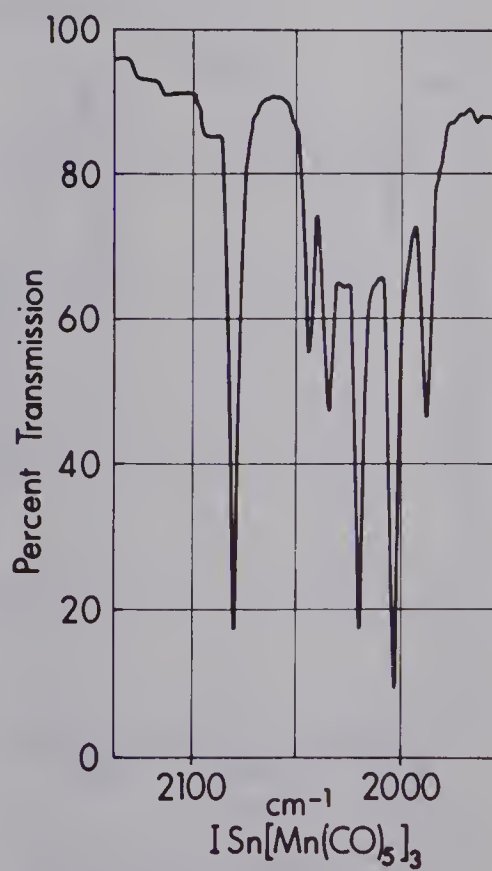


FIGURE 30

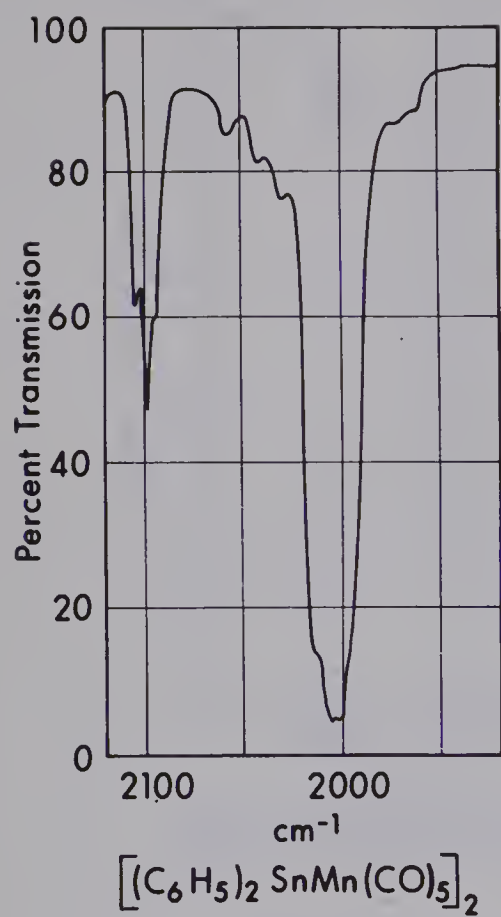


FIGURE 31

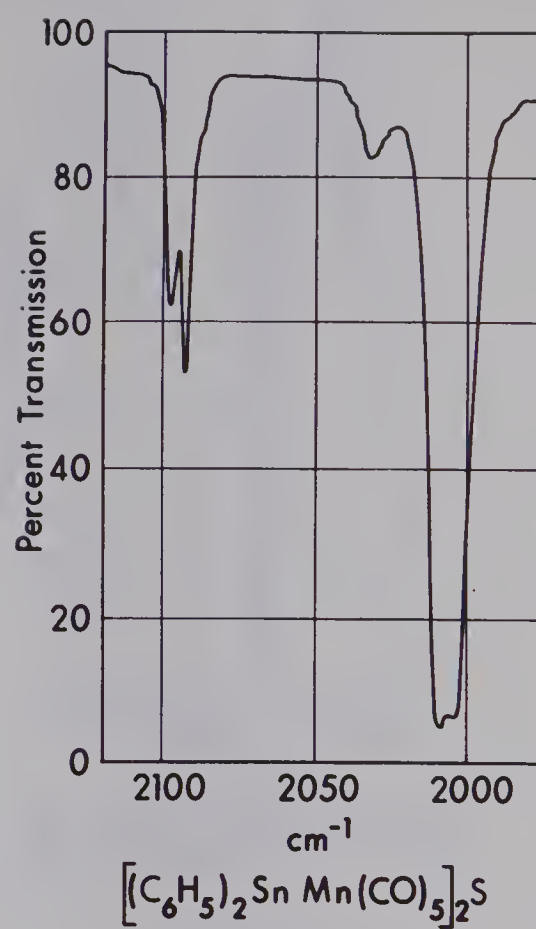


FIGURE 32

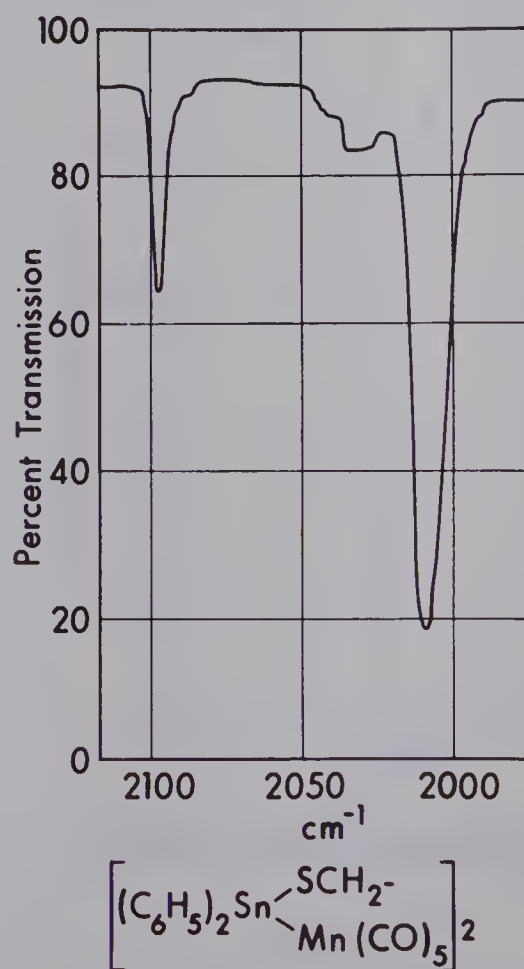


FIGURE 33

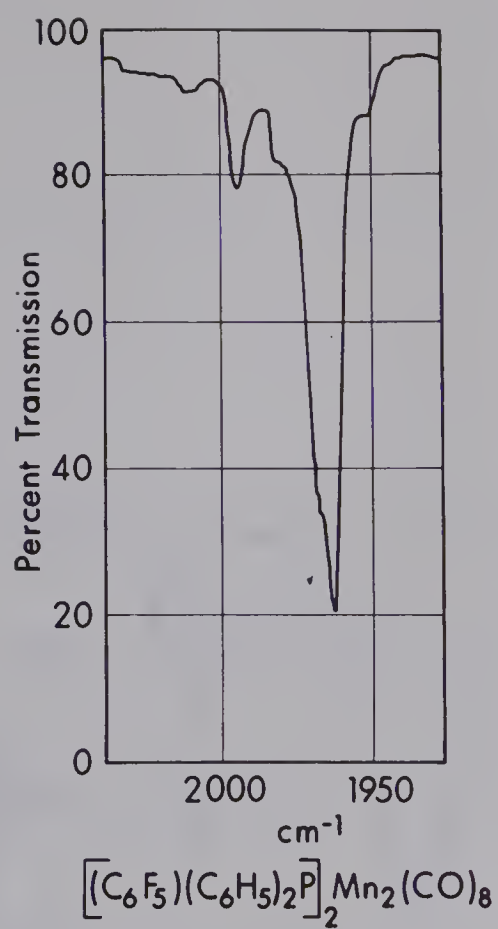


FIGURE 34

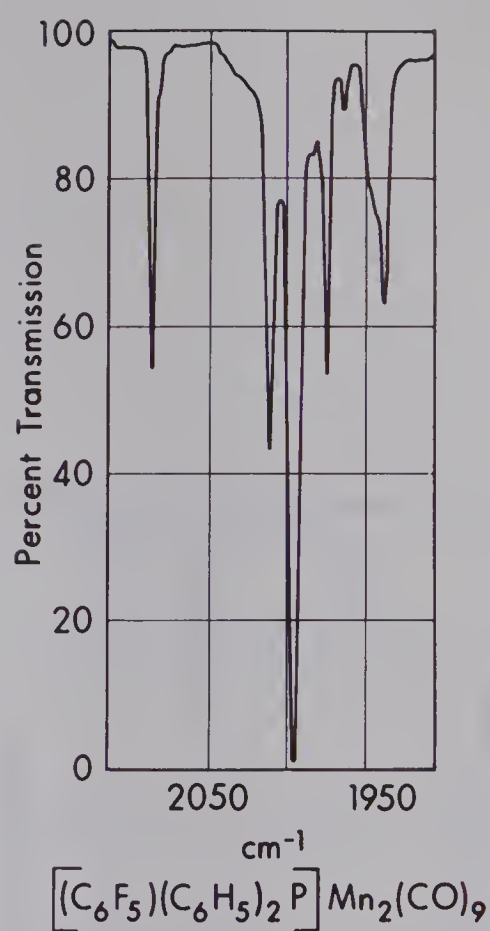


FIGURE 35

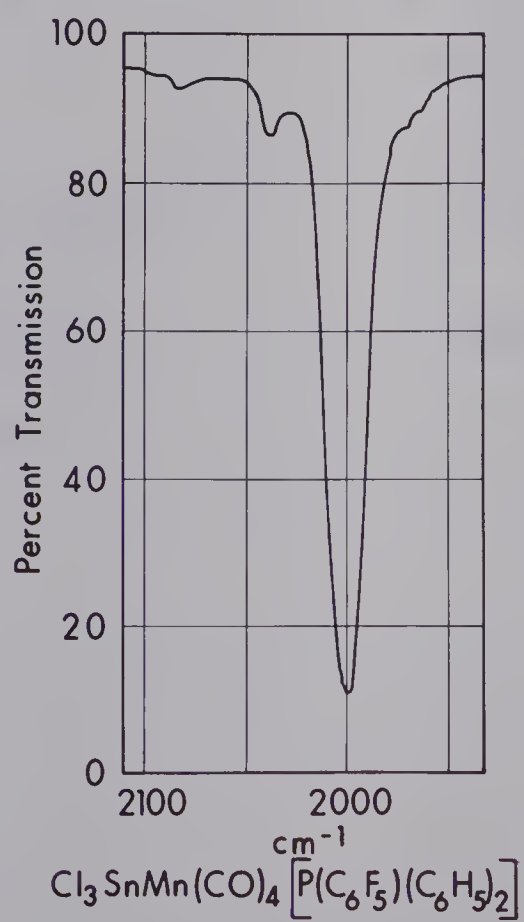


FIGURE 36

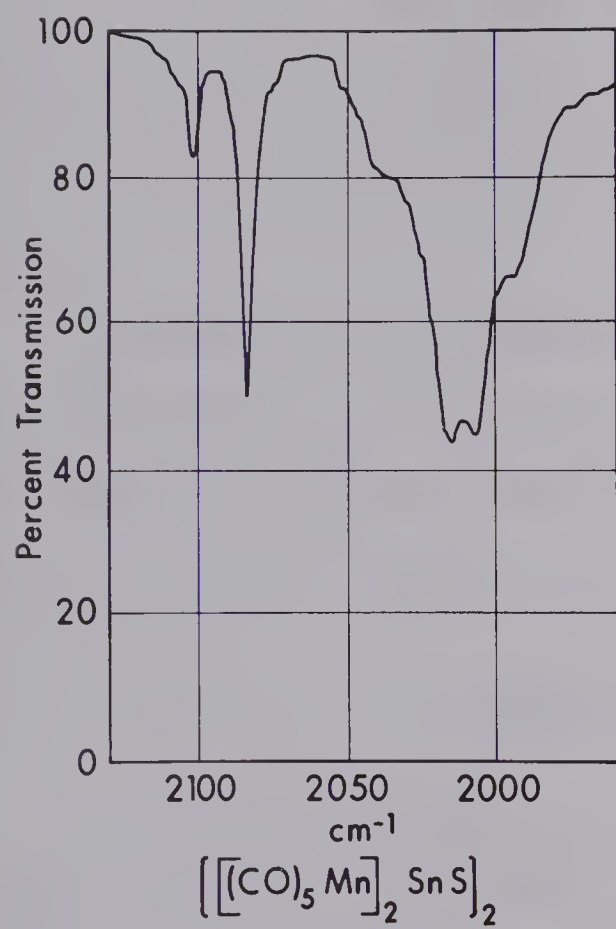


FIGURE 37

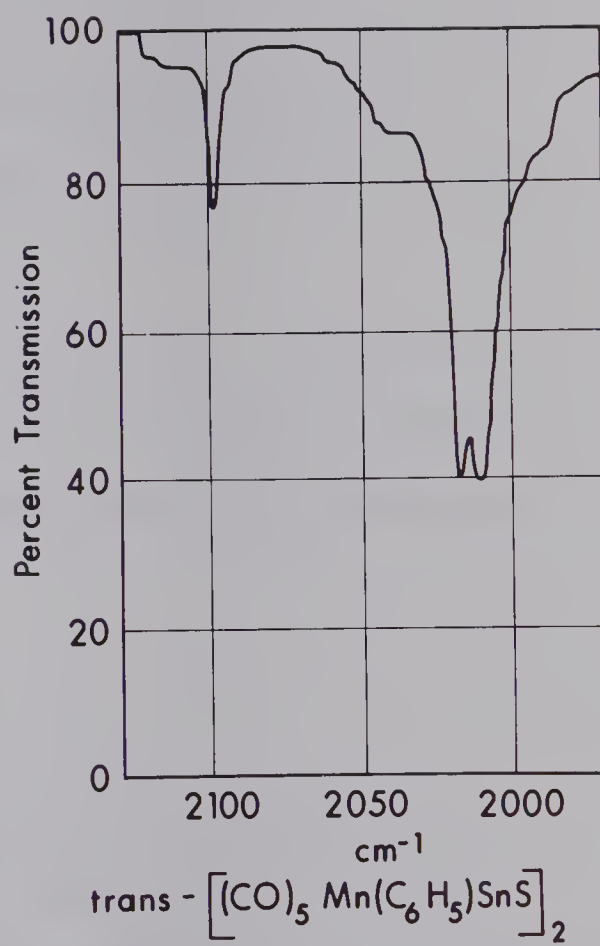


FIGURE 38

CHAPTER VIII

NMR STUDIES OF METHYLTIN AND METHYLTHIOTIN DERIVATIVES

In this chapter the results of proton nmr studies done on the methyl- and methylthiotin compounds prepared in this work are presented. The values obtained for the chemical shifts and proton-tin coupling constants are qualitatively discussed in the light of presently accepted theory.

It should also be pointed out here that ^{19}F nmr data were obtained for the C_6F_5 derivatives described earlier. The results of these studies are reported in the Dissertation of Dr. M. G. Hogben (113).

INTRODUCTION

Methyltin compounds are well suited to study using nuclear magnetic resonance methods. Besides the single, sharp signals obtained from the equivalent methyl protons, satellites due to proton-tin spin-spin coupling are also observed.

There are three isotopes of tin which have non-zero magnetic moments, ^{115}Sn (0.35% natural abundance), ^{117}Sn (7.67%) and ^{119}Sn (8.68%) (139). In each case the spin number of the nucleus is one-half and thus the nuclei have no quadrupole moments. In practice, only signals of the two more abundant isotopes are detected and used.

Splitting of the proton signal due to these two isotopes of tin appears as two sets of satellites at higher and lower field with respect to the central peak. The coupling constants, $J(^{117}\text{Sn}-\text{CH}_3)$ and $J(^{119}\text{Sn}-\text{CH}_3)$ have been found to vary, for four-coordinate tin compounds, over an approximate range of 50 to 100 cycles per second (cps).

Tin-proton coupling constants have become important as a means of predicting the degree of s character in the hybrid orbitals involved in the carbon-tin bonds. It has been found (140,141) that the values of J are sensitive to the electronegativity of substituents on tin.

Rehybridization of SP^3 orbitals on tetrahedral carbon as a result of varying electronegativity of substituent groups was first discussed by Bent (142) in 1960. In the so-called "Bent's Rule", it was stated that "the s character of an atom tends to concentrate in orbitals that are directed toward electropositive groups". This is illustrated by a system such as stannane (SnH_4). The central atom is considered to have four equivalent SP^3 hybrid orbitals, each with 25% s character. If one of the hydrogen atoms is replaced by an atom or group, X, of greater electronegativity, the change will cause the central atom to rehybridize slightly so as to shift some of its s character from X to the remaining carbon-hydrogen bonds.

Spin-spin coupling is generally considered to be the result of electronic effects. The Fermi contact contribution to the spin-spin coupling constant, J , between two nuclei is directly proportional to the product of the electron densities of the two bonding orbitals, through which they interact, at their respective nuclei. For atoms with hybridized bonding orbitals the electron density is proportional to the per cent s character in the hybridized atomic orbital used in forming the bond (140).

Holmes and Kaesz (140) found that considerable rehybridization in the tin atom of methyltin halides occurred as methyl groups in $(\text{CH}_3)_4\text{Sn}$ were replaced by chlorine atoms. This was indicated by a steady increase in $J(\text{Sn}-\text{CH}_3)$ which showed that s character was concentrating in the orbitals directed toward the remaining methyl groups. Because $^{13}\text{C}-\text{H}$ spin-spin interactions within the methyl groups remained nearly constant in the series of compounds investigated, these authors were able to assume that the carbon orbitals did not rehybridize appreciably.

In a series of methylstannanes, Flitcroft and Kaesz (141) found that progressive substitution of protons with methyl groups resulted in a decrease in $J(\text{Sn}-\text{H})$. Conversely, for $(\text{CH}_3)_4\text{Sn}$, the values of $J(\text{Sn}-\text{CH}_3)$ were at a minimum and increased progressively as protons were substituted up to $(\text{CH}_3)_3\text{SnH}$. It is apparent that these results are

also consistent with Bent's "rule".

Values of the chemical shift for methyltin compounds has been found to be in the range of 7-10 ppm relative to tetramethylsilane. It has been found (72,141) that addition of electronegative substituents results in a steady downfield shift in τ values due to deshielding of the proton nuclei.

RESULTS AND DISCUSSION

a. Methyltin Derivatives

The proton chemical shifts and coupling constants for these compounds are listed in Table XIII A. Figure 39 illustrates a typical spectrum with the methyltin satellites shown on an expanded scale.

Tetramethyltin, $(\text{CH}_3)_4\text{Sn}$, exhibits a chemical shift of 9.93 ppm (72) and coupling constants, $J(^{117}\text{Sn}-\text{CH}_3) = 51.5$ cps and $J(^{119}\text{Sn}-\text{CH}_3) = 54.0$ cps (142). Using the chemical shift value as a standard of comparison, Brown and Webster (72) established that the position of the methyl resonance shifts to lower field as methyl groups are replaced by chlorine atoms; a trend which may be regarded as an inductive withdrawal of shielding electron density by the chlorine atoms. A similar downfield shift is observed for the metal carbonyl derivatives of this work (see Table below). Taking the

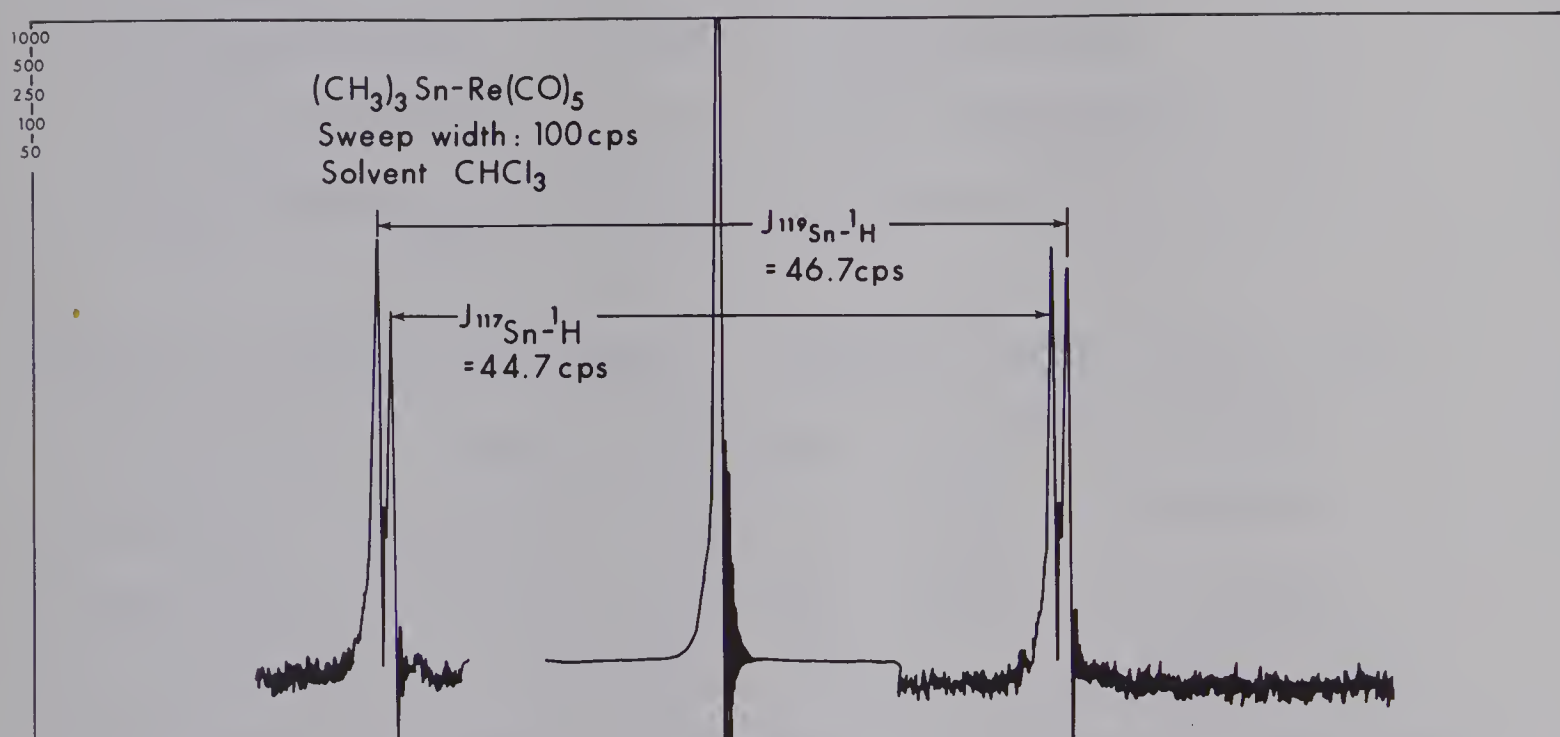


FIGURE 39: Expanded 100 Mc nmr spectrum of $(\text{CH}_3)_3\text{SnRe(CO)}_5$ showing Sn-119 and Sn-117 satellites.

<u>Compound</u>	<u>τ (CH₃)</u> (ppm)	<u>Compound</u>	<u>τ (CH₃)</u> (ppm)
(CH ₃) ₄ Sn	9.93	---	---
(CH ₃) ₃ SnRe(CO) ₅	9.58	(CH ₃) ₃ SnMn(CO) ₅	9.54
(CH ₃) ₂ Sn[Re(CO) ₅] ₂	9.14	(CH ₃) ₂ Sn[Mn(CO) ₅] ₂	9.17
CH ₃ Sn[Re(CO) ₅] ₃	8.43	CH ₃ Sn[Mn(CO) ₅] ₃	8.62

rhenium series as an example, chemical shift values range from 9.54 to 8.43 ppm as the number of Re(CO)₅ groups increases. This effect cannot be ascribed to electronegativity as it can for halogens, since metal carbonyl groups are usually considered to be electropositive. The reason for this anomaly (an upfield shift would be expected) is not clear but possibly lies in the multiple bond nature of the Sn-transition metal linkage. Similar downfield shifts have been observed for a series of M(CO)₃ (π -C₅H₅) (M = Mo, W) and Co(CO)₄ derivatives (14,43).

Turning now to the proton-tin coupling constants, again with (CH₃)₄Sn for comparison, it is seen from the following data that Bent's "rule" (142) is applicable. All J values (here J refers to ¹¹⁹Sn-CH₃ only) are lower than for tetramethyltin, the highest value of 48.3 cps being found for (CH₃)₃SnMn(CO)₅ and decreasing to approximately 24 cps for the tris derivative. This would be in accord

	Compound	$\tau(\text{CH}_3)$ (ppm)	$J(^{119}\text{Sn}-\text{CH}_3)$ (cps)
Decreasing	CH_3SnCl_3 *	8.35	100.0
electro-	$(\text{CH}_3)_2\text{SnCl}_2$	8.84	71.0
negativity	$(\text{CH}_3)_3\text{SnCl}$	9.37	59.7
of substi-	$(\text{CH}_3)_4\text{Sn}$	9.93	54.0
tuent	$(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$	9.54	48.3
other than	$(\text{CH}_3)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$	9.17	36.7
CH_3 .	$\downarrow \text{CH}_3\text{Sn}[\text{Mn}(\text{CO})_5]_3$	8.62	24

* Data for methyltin chlorides obtained from Ref.'s 72 and 143.

with the electropositive nature of the $\text{Mn}(\text{CO})_5$ groups, i.e., the values of J decrease because s character is concentrating in the Sn-Mn bond.

Values of J for $\text{Re}(\text{CO})_5$ analogs do not differ appreciably, but the difference is significant for corresponding $\text{Co}(\text{CO})_4$ compounds (43): $(\text{CH}_3)_3\text{SnCo}(\text{CO})_4$, 52.6 cps; $(\text{CH}_3)_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, 45.7 cps; $\text{CH}_3\text{Sn}[\text{Co}(\text{CO})_4]_3$, 33 cps. If the electronegativity is that overall property of a substituent that governs J , one may conclude that the $\text{Co}(\text{CO})_4$ group is more electronegative than $\text{Mn}(\text{CO})_5$ in these compounds. This is in harmony with the facts that $\text{HCo}(\text{CO})_4$ is a stronger acid than $\text{HMn}(\text{CO})_5$ (144) and that $[\text{Co}(\text{CO})_4]^-$ is a weaker nucleophile than $[\text{Mn}(\text{CO})_5]^-$ (145,146).

As is noted in Table XIII A, spectra of the $\text{Re}(\text{CO})_5$ derivatives of $(\text{CH}_3)_3\text{Sn}-$, $(\text{CH}_3)_2\text{Sn}-$ and $\text{CH}_3\text{Sn}-$ and of the compound $\text{CH}_3\text{Sn}[\text{Mn}(\text{CO})_3]_5$ were obtained in pyridine. This was necessary in the case of the two tris derivatives to achieve sufficient solubility for nmr studies. At the same time, this raised the possibility that pyridine would influence J (values would increase) by coordination to tin (this has been observed by Maddox et al. (147)). As a control, J values for $(\text{CH}_3)_3\text{SnRe}(\text{CO})_5$ and $(\text{CH}_3)_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ were measured so that valid comparisons with the tris derivatives could be made. The results agreed with values measured in CDCl_3 and CHCl_3 and enabled one to conclude that tin has no appreciable acceptor properties in these compounds.

b. Methylthiotin Derivatives

The chemical shifts and proton-tin coupling constants for the seven methylthiotin derivatives are shown in Table XIII B. Figures 40 and 41 show representative spectra for two of these compounds.

The $(\text{CH}_3\text{S})_3\text{Sn}$ derivatives exhibit greater downfield shifts for the methylthio proton when compared with the $(\text{CH}_3)_3\text{Sn}$ compounds. A similar observation for the bis and tris derivatives can be made. The downfield shifts can be attributed to a large extent to deshielding by the electronegative sulfur atoms.

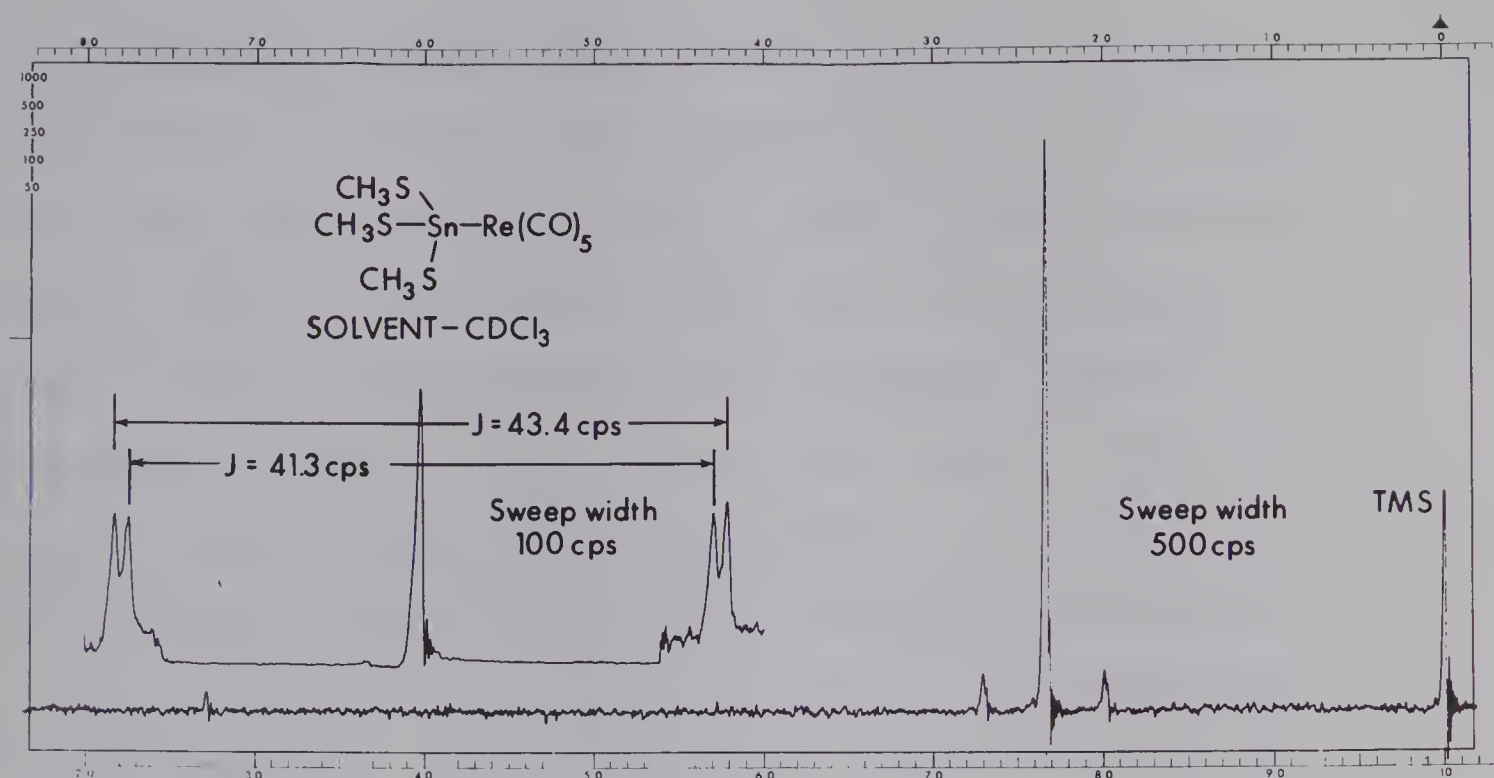


FIGURE 40

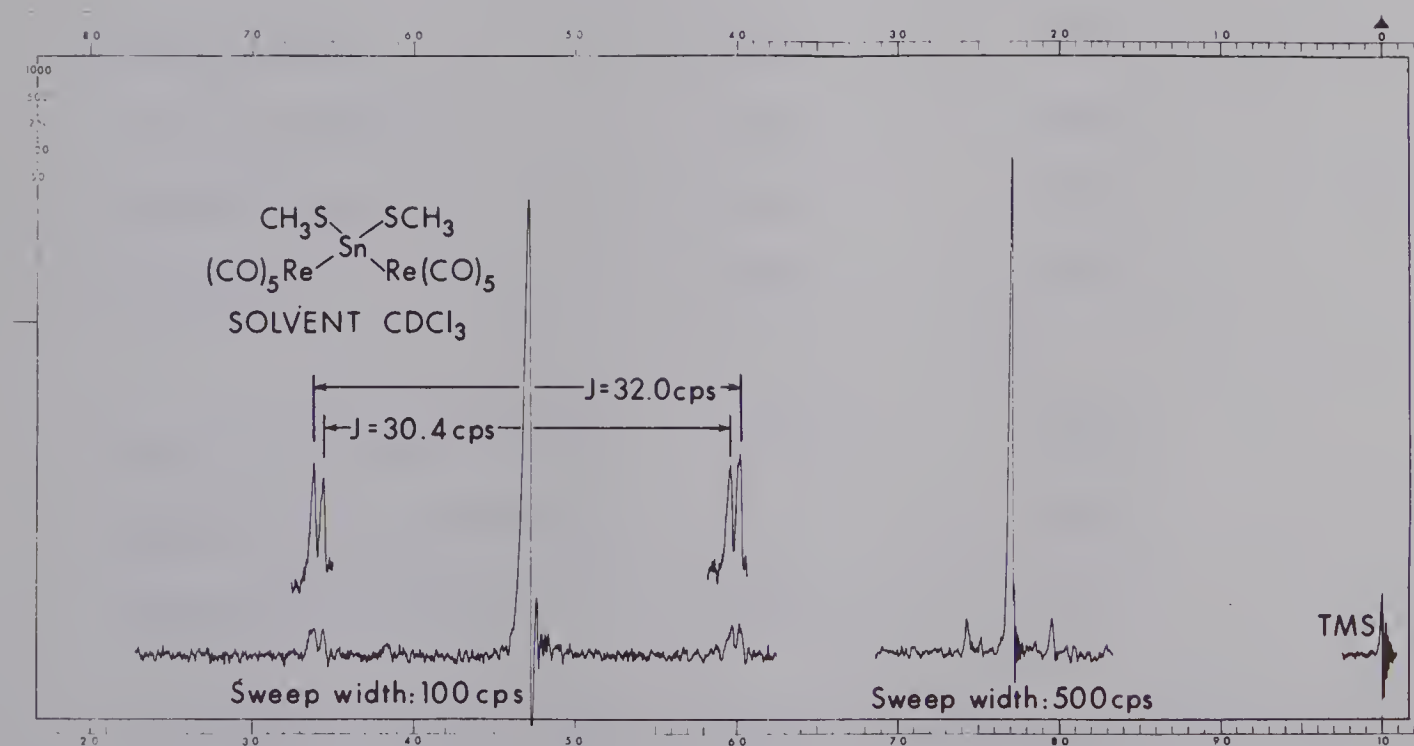


FIGURE 41

Recently, related, independent studies involving compounds of the type $(\text{CH}_3)_n\text{Sn}(\text{SCH}_3)_{4-n}$ ($n = 0-4$) have been reported by Abel and Brady (148) and Van den Berghe et al. (149). Both groups showed that the methyltin proton shifts increased with an increasing number of methylthio groups. Also, as has been found in this work for the series $(\text{C}_6\text{H}_5)_n(\text{CH}_3\text{S})_{3-n}\text{SnMn}(\text{CO})_5$ ($n = 0, 1, 2$), an increasing downfield shift of the methylthio protons as the number of CH_3S groups increased is apparent (see table below).

<u>Compound (Ref. 148)</u>	<u>$\tau(\text{CH}_3\text{S})$</u>	<u>$J(^{119}\text{Sn}-\text{SCH}_3)$</u>
	ppm	cps
$(\text{CH}_3)_3\text{SnSCH}_3$	8.00	37.5
$(\text{CH}_3)_2\text{Sn}(\text{SCH}_3)_2$	7.84	44.2
$\text{CH}_3\text{Sn}(\text{SCH}_3)_3$	7.73	56.7
$\text{Sn}(\text{SCH}_3)_4$	7.68	66.0
$(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{S})\text{SnMn}(\text{CO})_5$	7.95	39.4
$(\text{C}_6\text{H}_5)(\text{CH}_3\text{S})_2\text{SnMn}(\text{CO})_5$	7.74	40.8
$(\text{CH}_3\text{S})_3\text{SnMn}(\text{CO})_5$	7.62	45.9

An effect of the sulfur atoms is reflected also in the values of $J(\text{Sn}-\text{SCH}_3)$ which are only slightly less ($\sim 3\text{cps}$) than the corresponding methyltin series and are

perhaps somewhat higher than would be expected a priori, considering that the protons are one atom further removed from tin. Furthermore, as previous workers (148,149) found, J values increased with progressive addition of methylthio groups, as shown in the preceding table. Abel and Brady (148) have attributed this effect to a steady enhancement of the electron density in the Sn-S bonds with increasing methylthio content; they further speculate that this may be due to an increase in Sn-S π -bonding with increasing numbers of methylthio groups.

J(Sn-SCH₃) values are uniformly lower for the metal carbonyl derivatives than for the organotin derivatives. For example, J(¹¹⁹Sn-SCH₃) is 56.7 cps for (CH₃S)₃SnCH₃, a value about 10 cps higher than that for (CH₃S)₃SnMn(CO)₅ (45.9 cps). Here, as for the methyltinmanganese series, the difference can be attributed to the more electropositive character of the metal carbonyl moiety; i.e., there is a greater concentration of s character in the tin orbitals directed toward the transition metal.

EXPERIMENTAL SECTION

Spectra were obtained using Varian A-60, A-56/60 and HA-100 instruments operated by technical staff.

Samples were prepared by dissolving approximately

100 mg of the material in CDCl_3 or CHCl_3 with tetramethylsilane added as an internal standard. All spectra, with the exception of $\text{CH}_3\text{Sn}[\text{Mn}(\text{CO})_5]_3$, were obtained at the ambient temperature.

TABLE XIII

PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS

FOR METHYLTIN AND METHYLTHIOTIN DERIVATIVES

A. METHYLTIN DERIVATIVES

Compound	Solvent	$\tau^a(\text{CH}_3)$	$J(^{117}\text{Sn}-\text{CH}_3)$ cps	$J(^{119}\text{Sn}-\text{CH}_3)$ cps
$(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$	CDCl_3	9.54	46.2	48.3
$(\text{CH}_3)_3\text{SnRe}(\text{CO})_5$	CHCl_3	9.58	44.7	46.7
	pyridine	9.29	44.3	46.3
$(\text{CH}_3)_2\text{ClSnMn}(\text{CO})_5$	CDCl_3	9.06	43.9	45.8
$(\text{CH}_3)_2(\text{C}_6\text{H}_5\text{S})\text{SnMn}(\text{CO})_5$	CDCl_3	9.37	42.8	45.4
$(\text{CH}_3)_2(\text{C}_6\text{F}_5\text{S})\text{SnMn}(\text{CO})_5$	CDCl_3	9.30	42.7	44.6
$(\text{CH}_3)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$	CDCl_3	9.17	34.9	36.7
$(\text{CH}_3)_2\text{Sn}[\text{Re}(\text{CO})_5]_2$	CDCl_3	9.14	34.9	36.7
	pyridine	9.13	34.8	36.3
$\text{CH}_3\text{Sn}[\text{Mn}(\text{CO})_5]_3$	pyridine ^b	8.62		$\sim 24^c$
$\text{CH}_3\text{Sn}[\text{Re}(\text{CO})_5]_3$	pyridine	8.43		24.7^d

TABLE XIII (continued)

B. METHYLTHIOTIN DERIVATIVES^e

Compound	τ^a (CH ₃)	J (¹¹⁷ Sn-SCH ₃) cps	J (¹¹⁹ Sn-CH ₃) cps
(CH ₃ S) ₃ SnMn(CO) ₅	7.62	43.8	45.9
(CH ₃ S) ₃ SnRe(CO) ₅	7.67	41.3	43.4
(CH ₃ S) ₂ Sn[Mn(CO) ₅] ₂	7.61	31.8	33.0
(CH ₃ S) ₂ Sn[Re(CO) ₅] ₂	7.70	30.4	32.0
(CH ₃ S)Sn[Mn(CO) ₅] ₃	7.84	----- ^f	----- ^f
(C ₆ H ₅) ₂ (CH ₃ S)SnMn(CO) ₅	7.95	37.8	39.4
(C ₆ H ₅)(CH ₃ S) ₂ SnMn(CO) ₅	7.74	39.8	40.8

a. Chemical shift in ppm relative to (CH₃)₄Si.

b. Measured at 55° for increased solubility.

c. Average value: ¹¹⁷Sn and ¹¹⁹Sn satellites not resolved.

d. ¹¹⁷Sn and ¹¹⁹Sn couplings not resolved. Low solubility necessitated use of Varian time-averaging computer and several scans.

e. All spectra measured in CDCl₃.

f. Not obtainable because of insolubility and instability of compound.

CONCLUSIONS

In this Dissertation, the synthesis of a number of new, and in some cases quite novel, compounds containing metal-metal bonds has been reported. Although a few derivatives of organotin compounds having two or three manganese or rhenium carbonyl groups were known prior to this work, they had not been well-characterized. It has been shown here that compounds of the types $R_2Sn[M(CO)_5]_2$ and $RSn[M(CO)_5]_3$, where R represents a wide range of halogens and organic groups, can be prepared by straightforward reactions.

The much greater stability of Sn-Mn and Sn-Re bonds compared to Sn-Sn bonds has been demonstrated by a number of cleavage reactions which left the metal-metal bond intact. Replacement of halogens by C_6F_5Li or C_6F_5MgBr resulted in the first known C_6F_5Sn compounds containing metal carbonyl groups while reaction of $R_nCl_{3-n}SnM(CO)_5$ with various thiols gave a wide range of stable, crystalline alkyl- and arylthiotin derivatives. In most cases the metal-metal bond was preserved.

A number of novel ditin species were obtained in this work. The compound, $[(C_6H_5)_2SnMn(CO)_5]_2$, is one of the few known cases of a four-metal chain. Reaction of dichlorotin-manganese derivatives with sodium sulfide yielded highly inert compounds where tin atoms were

presumed to be bridged by sulfur atoms.

Infrared studies were highly informative. Calculation of the carbonyl stretching force constants for the mono (metal carbonyl) derivatives indicated that the Cl_3Sn group is a strong π -acceptor. From spectra of the bis- and tris-derivatives it was concluded that coupling of the stretching modes through tin must be invoked to explain the number of observed bands. Moreover, this coupling was observed across four or five atoms in the systems OC-Mn-Sn-Sn-Mn-CO and $\text{OC-Mn-Sn-S-Sn-Mn-CO}$ but not, however, in the $\text{OC-Mn-Sn-S-CH}_2\text{-CH}_2\text{-S-Sn-Mn-CO}$ system. This coupling is attributed to d-electron interactions.

Nmr spectra of the methyltin and methylthiotin derivatives were obtained. The trend to lower values for $J(\text{Sn-CH}_3)$ with an increasing number of $\text{M}(\text{CO})_5$ groups was taken to suggest that s character was concentrating toward the more electropositive metal carbonyl group(s).

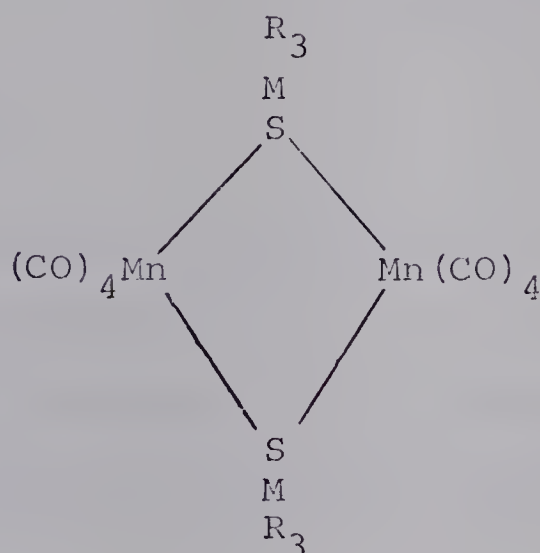
SUGGESTIONS FOR FUTURE INVESTIGATIONS

The work presented here has brought to light a number of interesting possibilities for future research, mainly from the synthetic standpoint. Those which might lead to some interesting new derivatives of tin and/or the carbonyls of rhenium and manganese are listed here:

- Using the compounds $(C_6H_5)_3SnSLi$ and $(C_6H_5)_3GeSLi$ (150,151) and $R_nCl_{3-n}SnMn(CO)_5$, derivatives of the type $[(C_6H_5)_3MS]_nR_{3-n}SnMn(CO)_5$ may be prepared:



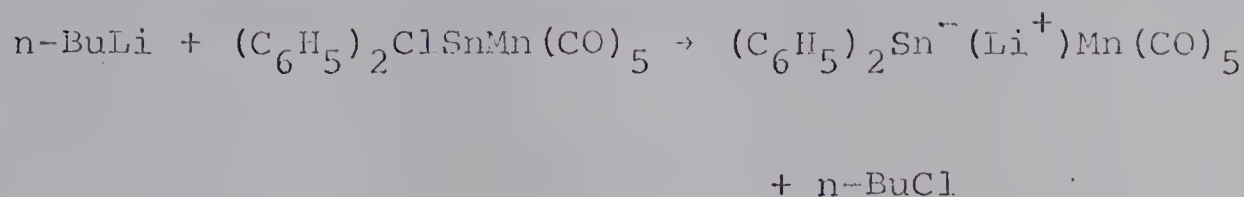
- The same lithio compounds may also react with $BrM'(CO)_5$ ($M' = Re, Mn$) to provide the species $(C_6H_5)_3MSM'(CO)_5$. This product might then dimerize to yield compounds of the type $[(CO)_4M'SM(C_6H_5)_3]_2$ which would possess R_3MS bridges to the transition metal atoms:



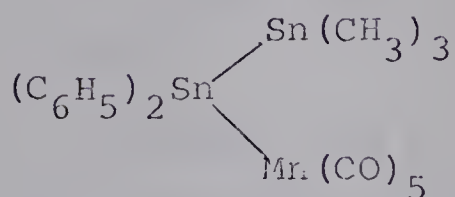
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- In the discussion of the compound $[(C_6H_5)_2SnMn(CO)_5]_2$ (Chapter IV), a lithio-tin intermediate was postulated. It is quite feasible that this and related intermediates might be obtained from a transmetallation reaction

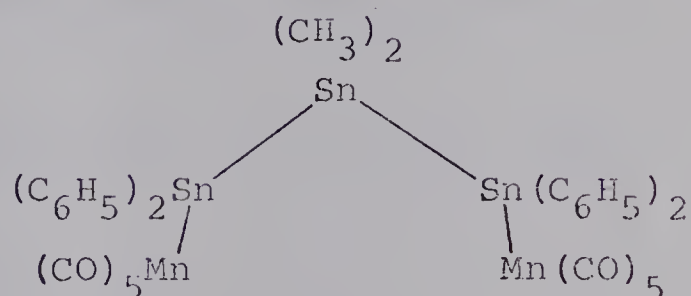
using n-butyllithium:



Reaction of the intermediate with organotin halides might provide routes to novel metal-metal bond compounds such as:



and



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XL

4. Finally, a greater insight into the nature of bonding in the compounds described in this Dissertation may be obtained by spectroscopic studies using the far-infrared, Raman and Mössbauer resonance techniques.

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